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THE ELECTRICAL RESISTANCE OF METALS UNDER

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BY P. W. BRIDGMAN.

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# THE ELECTRICAL RESISTANCE OF METALS UNDER PRESSURE.

## BY P. W. BRIDGMAN.

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#### Introduction.

In this paper the effect of pressure combined with temperature on the electrical resistance of 22 metals is investigated. The list of metals includes nearly all that are sufficiently permanent in the atmosphere and can be made into wire. The pressure range is from atmospheric pressure to 12000 kg. per cm.², and the temperature range from 0° to 100°.

The subject is one of considerable importance for the electron theory of metals. Previous discussion has been concerned mostly with explaining the effect of temperature on resistance, and very little with the effect of pressure. There seems to be no reason for this except the lack of experimental material; the pressure effect is certainly as significant as the temperature effect, and a study

of it should throw much additional light on the mechanism. The old form of electron theory due to Drude was not competent to explain the pressure effect, although it dealt fairly well with the temperature effect. If the experimental facts with regard to pressure had been sufficiently known it would not have required considerations of specific heat to show that Drude's theory cannot be correct. Only quite recently has the theoretical bearing of the effect of pressure begun to be discussed 1. I hope in this paper to present enough material for a more extended discussion, and in the latter part of the paper I shall try to indicate some of the significance Even in its present incomplete form, however, the electron theory will evidently need other data than the effect of pressure and temperature on resistance. One of the most important of such other effects is that of pressure on thermo-electromotive force; I hope to give such data in a succeeding paper for some of the metals investigated here.

The effect of pressure on electrical resistance has of course been measured a number of times before. The data here cover a considerably wider range, both of material and pressure. None of the previous work covers a pressure range of more than 3000 kg., and except for a single isolated instance with 100% error, I know of no measurements of the variation of pressure coefficient with temperature. The data here bring out the to me unexpected fact that the variation of pressure coefficient with temperature is very much less than the variation of resistance itself. I have also tried to improve on previous work in respect to the purity of the materials. Where possible I have given chemical analyses, and in all cases the temperature coefficient. The temperature coefficient is a very good indication of the purity of the metal, being almost always higher for the purer material. The pressure coefficient shows no such consistent variation, but may sometimes increase and sometimes decrease in the presence of impurity.

The most important previous work on the effect of pressure has been done by Lisell <sup>2</sup> up to 3000 kg., Lafay <sup>3</sup> to 2000 kg., Barus <sup>4</sup>

<sup>1</sup> E. Grüneisen, Verh. D. Phys. Ges. 15, 186-200 (1913).

<sup>2</sup> E. Lisell, Om Tryckets Inflytande på det Elektriska Ledningsmotståndet hos Metaller samt en Ny Metod att Mäta Höga Tryck, Upsala, (1902).

3 Lafay, Ann. de Chim. et Phys. 19, 289–296 (1910). C. R. 149, 506–569,

<sup>(1909).</sup> <sup>4</sup> C. Barus, Bull. U. S. Geol. Sur. No. 92 (1892). Amer. Jour. Sci. **40**, 219 (1890).

and Palmer<sup>5</sup> to 2000 kg., and Beckman<sup>6</sup> with Lisell's apparatus. For a full bibliography the papers of Lisell and Beckmann may be consulted.

The plan of this paper is to first give the data for individual substances with a description of the details of preparation and the characteristic features of each substance, and then a discussion of the significance of the results.

#### EXPERIMENTAL METHODS.

The apparatus is in all essentials the same as that previously used and described in a number of papers 7. It consists of two parts, an upper and a lower cylinder connected by a stout tube. In the upper cylinder pressure is produced by the descent of a piston driven by a ram. The upper cylinder also contains the coil of manganin wire which gives the pressure by its change of resistance. The calibration of the manganin coil and the details of the upper cylinder have already been fully described. During the experiment, the upper cylinder was kept thermostatically at a constant temperature of 40°. The lower cylinder contains the metal whose resistance is to be measured, and is placed in a second thermostat independent of that controlling the upper cylinder. The resistance of the lower coil was measured on the same Carey Foster bridge as was the manganin wire; connection to the bridge was by mercury switches in paraffine blocks. The lower cylinder is shown in Figure 1. It consists of a cylindrical piece of Chrome Vanadium steel pierced axially with a  $\frac{9}{16}$  inch hole, enlarged and threaded to receive the connecting pipe at one end and at the other the plug through which the insulating leads connect with the wire under measurement. Lower cylinders of two different lengths were used according as the wire to be measured was insulated, and so could be coiled into a narrow space, or was bare and had to be wound in the spiral

(e) Phys. Zs. 16, 59-62 (1915).

<sup>5</sup> A. deF. Palmer, Amer. Jour. Sci. 4, 1, (1897) and 6, 451 (1898).

<sup>6</sup> B. Beckman, (a) Inaug. Dis. Upsala, (1911).
(b) Ark, f. Mat., Astr., och Fys. 7, No. 42, (1912).
(c) Ann. Phys. 46, 481–502 (1915).
(d) Ann. Phys. 46, 931–941 (1915).

<sup>7</sup> P. W. Bridgman, Proc. Amer. Acad. 47, 321-343 (1911), and 49, 627-643 (1914).

grooves of a core about 9 cm. long. The usual accidents were encountered in making these cylinders; several broke during use because of defective steel.

It was my original intention to make several apertures in the lower cylinder, so that measurements could be made on several coils at once, but this scheme was given up because two such cylinders, after much work had been put on them, proved defective. It seems to be the part of experimental economy when much effort in making the apparatus may go for nothing because of defective material, to make the apparatus of as simple design as possible, even at the expense of extra labor in obtaining the readings. Positive results were obtained with one of these preliminary cylinders, however,

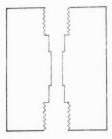


FIGURE 1. The cylinder to contain the wire under measurement. At the top, connection is made to the pressure pump; at the bottom, the insulating plug with the wire is inserted.

in which two coils could be placed simultaneously. Measurements were made on two coils of iron, and at another time on two coils of copper. The agreement between the members of these two pairs of coils was perfect within the sensitiveness of the measurements, which for these coils was about 1/3000 of the change of resistance. This is gratifying because it shows that the effect of pressure on resistance may be reproduced with not more error than that in the absolute measurement of pressure.

The resistance was measured by a null method on a Carey Foster bridge. The galvanometer circuit was permanently closed to avoid thermo-electric effects, and the battery circuit was closed only when making measurements. The current was, however, kept so low that the battery circuit could be kept permanently closed with no change

of resistance due to heating. It should be emphasized that this avoids a source of error present in the work of Lisell <sup>2</sup> and Beckman. <sup>6</sup> They allowed the current to flow continuously through the wire. Any change in the thermal conductivity of the oil under pressure would change the heating effect and so partly mask the change of resistance due to pressure. If thermal conductivity of a liquid decreases under pressure, as seems plausible, this source of error would make their pressure coefficient too low; which as a matter of fact is the direction of discrepancy between most of their results and mine. The magnitude of the error from this source varies with the material and the size of the wire. Lisell states that for lead his error from this source is probably not as much as 1%, but for zinc he is willing to admit the probability of an error as large as 10%. Beckman, working with Lisell's apparatus, makes no mention of this source of error, and

would seem not to have sufficiently guarded against it.

Temperature control was one of the most troublesome difficulties of the preliminary work. The effect of temperature on resistance is very large compared with that of pressure; for some substances 1° C may make a change in resistance 3000 or 4000 times as large as 1 kg. pressure. The upper thermostat in which was the manganin measuring coil gave no trouble; it was sufficient to keep the temperature of this within 1°. For the lower thermostat a bath of water violently stirred was used, with a very sensitive regulator consisting of a spiral of thin walled copper tubing filled with ethyl benzoate and connected to a regulating mercury column in a glass capillary by means of a steel intermediary part to which the copper was soldered and in which the glass was directly sealed without cement. By means of a Beckmann thermometer and adjustment by hand of the mercury contact if necessary, temperature could be kept constant within two or three thousandths of a degree during a run. Error from slow drift was avoided in those cases where the temperature coefficient was high compared with the pressure coefficient by using as the comparison coil another coil of the same substance and resistance as the coil subjected to pressure, placed in a glass tube in the bath in close proximity to the cylinder. For those substances with larger pressure coefficient this precaution was not necessary, but a comparison coil of manganin at room temperature was sufficiently good. Of course the temperature of 0.0° was obtained in an ice bath, and no temperature trouble was ever found here. Difficulty of temperature control probably accounts for the fact that most previous measurements have been made only at 0.0°. It was not possible to run the thermostat with water at 100°. Instead, the maximum temperature was usually set at about 99° and troublesome evaporation avoided by covering the surface with a thin layer of oil.

The manganin resistance gauge was calibrated from time to time during the measurements, which extended over six months after the preliminary work. There was a slow and uniform secular change in the constant of the coil amounting in all to about  $\frac{2}{3}\%$ . Of course correction was made for this change. A new detail in the method of calibration gave somewhat sharper results than possible by the method described in the previous paper. By using petroleum ether to transmit pressure to the freezing mercury instead of kerosene, it is possible to avoid any effects due to viscosity of the transmitting medium, and obtain results more quickly and sharply. The freezing pressure of mercury at  $0.0^{\circ}$  may be reached from either above or below within the limits of sensitiveness, about 1/3500, in fifteen minutes. The manganin slide wire of the Carey Foster bridge was also repeatedly calibrated. This showed a secular change, due to wear, of about  $\frac{1}{2}\%$  during the six months of the runs.

The wires to be experimented on were usually wound either noninductively on themselves in the form of anchor rings of approximately 1.5 cm. external diameter, or were wound non-inductively in a double thread cut on a bone core. It is essential that the method of winding be such that the pressure is transmitted freely to all parts of the coil without any mechanical hindrance from the frame on which it is wound. This object is obviously at once attained when the wire is wound on itself without a core, constrained only by a wrapping of silk thread to keep it in shape, but this method is feasible only when the wire can be covered with silk insulation without damage. If the wire is soft like lead, it cannot be covered without damage, and it must be wound bare on some sort of a core. Several attempts were made before a suitable material for a core was found. At first, hard rubber was used, but this is so compressible that at the highest pressures the wire drops out of the grooves, and is so expansible that at the highest temperatures the wire is stretched. A hard rubber shell on a steel core does not work because the unequal compressibility of the rubber and steel causes the rubber to crack. Bakelite was tried without success. I was afraid to use mica because of the sharp bends unavoidably introduced into the wire during handling. Finally bone was found to be satisfactory from the points of view of both sufficiently low compressibility and thermal expansion. A double 12 or 18 thread of square section was cut in the lathe on the surface of a cylinder

1.7 cm. diameter and 9 cm. long, and the wire was wound loosely in the groove.

Another mechanical effect apart from that offered by the constraints is due to the viscosity of the transmitting medium. This was of course particularly prominent at low temperatures. It may be almost entirely avoided by using petroleum ether to transmit pressure at 0° and 25°. At higher temperatures, pure kerosene may be used without sensible error.

When these various precautions have been taken to avoid extraneous mechanical and temperature effects, results may be obtained of a constancy and regularity much greater than I had anticipated. In the majority of cases pressure could be applied to 12000 kg. and removed with a change of zero of less than 0.3% of the total change, or a constancy of the total resistance of 0.01%, and in many cases the change was imperceptible. This change was not the effect of pressure alone, but was the sum of all effects, including temperature drift in the thermostat and changes in the bridge due to changes in room temperature. Nevertheless, 0.3% of the change might be 15 or 20 times the sensitiveness of the measurements, and in all such cases a correction for the zero drift was applied proportional to the time.

The wires were attached to the terminals of the insulating plug with silver solder in most cases where the melting point was high enough; the softer metals were attached usually with soft solder. In a few cases other methods of contacting were employed, which will be described in detail later. In all cases in which metallic connection can be made by fusing, there need be no trouble whatever at the con-

tacts.

Other minor corrections are for the effect of pressure on the leads of the insulating plug (only 0.2 mm. of bridge wire at the maximum) and a temperature correction for the leads, which was determined experimentally, and the correction for lack of uniformity of the bridge wire.

The purity of the metals used is a matter of great importance. The harder metals were drawn from sizes below 0.04 inch through diamond dies. Before passing to the diamond dies the trace of iron that might have been rubbed in from the larger steel dies was removed by etching off with acid at least 8% of the diameter. Softer metals were extruded at one operation through a steel die. Special tests with the very delicate potassium thiocyanate method showed no perceptible iron introduced during the extrusion. Chemical analyses are given for all those metals for which I could obtain it. As giving the best indication

of the purity, careful measurements were made of the temperature coefficient. In many cases the materials seems purer than any on which measurements have been previously published. Detailed data from which the purity may be judged are given under the individual substances. The resistance at  $25^{\circ}$  intervals in terms of that at  $0^{\circ}$ C as unity is tabulated in the following. The average temperature coefficient between  $0^{\circ}$  and  $100^{\circ}$  may be read directly from the resistance at  $100^{\circ}$ .

In comparing these results with those of others it is necessary to keep in mind that the relation between resistance and temperature is not linear, but for most substances the resistance increases more rapidly at higher temperatures. This introduces a slight correction. For instance, Jaeger and Diesselhorst <sup>8</sup> made measurements at 18° and 100°, extrapolated linearly to find the resistance at 0°, and tabulated the coefficient obtained in this way as the average coefficient between 0° and 100°. The value thus found is evidently too high, and so is not strictly comparable with the results found here. The correction, which is always slight, may be computed in any case from the tables given below.

After winding the coils they were in most cases seasoned by exposing to several changes of temperature between 0° and 140° or 150° in an air bath. In addition to this, the coil was frequently seasoned for pressure by several times exposing to 12000 kg. This seasoning for pressure turned out to my surprise, however, to be hardly necessary. A number of substances showed no perceptible change of resistance after their first exposure to pressure. This is an interesting point, as it indicates with a high degree of sensitiveness the perfect elasticity of volume under hydrostatic pressure. Further details of seasoning are given under the individual substances.

Measurements of the change of resistance were made at intervals of 1000 kg. at 0°, 25°, 50°, 75°, and 100°. Two readings were made at the maximum and two zero readings, one before and one after the run. At each temperature, therefore, 15 readings were made. The straight line connecting the mean of the two points at 12000 with the mean zero was computed, and at each pressure the difference between the observed and computed value was found. These differences were then smoothed graphically.

Readings of resistance were made with increasing and decreasing

 $<sup>^8</sup>$  W. Jaeger und H. Diesselhorst, Phys. Tech. Reichsanstalt, Wiss. Abh.  $\pmb{3},$  269–425 (1900).

pressure in order to avoid any error due to the direction of change of pressure. These readings were made alternately; at 0, 1000, 2000, 4000, 6000, 8000, 10000, 12000, with increasing pressure, and at 12000, 11000, 9000, 7000, 5000, 3000, and 0 with decreasing pressure. There is no perceptible hysteresis. Figure 2 for lead shows this. This entire absence of hysteresis was very gratifying; I had not expected results so favorable. At the two lower temperatures of the earlier runs a small effect in a direction opposite to that of hystersis was sometimes found. This was traced to the viscosity of the kerosene transmitting pressure; it entirely disappeared on using the less viscous petroleum ether to transmit pressure at 0° and 25°.

After every change of pressure some time is necessary before the next reading can be made, because of temperature disturbance due to the heat of compression. This change of temperature is in many cases so great as to entirely mask the effect of change of pressure; immedi-

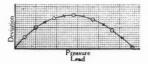


Figure 2. The deviation from linearity for lead against pressure, both on an arbitrary scale. The purpose of the diagram is to show the entire absence of hysteresis; the circles show the measurements with increasing pressure, and the crosses with decreasing pressure. One small division corresponds to \( \frac{1}{3} \)% of the total change of resistance produced by the maximum pressure.

ately after changing pressure the resistance of most substances changes in a direction opposite to that of the final change. Some substances, like lead, in which the ratio of pressure coefficient to temperature coefficient is high, do not show the initial reversal, but in most cases the immediate change may be 5 or 10 times as great as the final change and in the opposite direction. This effect is very troublesome, as it may need as much as 30 or 45 minutes to reach temperature equilibrium after each change of pressure. Without some trick of procedure a run at a single temperature might occupy seven or eight hours and is excessively tedious. The time to reach equilibrium may be very much shortened by running the pressure beyond the desired final mark and then, after most of the heat of compression has been dissipated, bringing the pressure back to the desired mark. The heating effect during this second change of pressure is opposite in direction from the

initial change. With a little practice a secondary change of such magnitude may be found that temperature equilibrium is reached in 5 to 7 minutes.

When the apparatus was in good running order and the thermostat had reached equilibrium, a complete run on one substance at one temperature could usually be made in about two hours. Including all manipulations of adjusting temperature of the thermostat and waiting for zero equilibrium, runs at two different temperatures could be easily made on a single substance in a working day.

#### GENERAL CHARACTER OF RESULTS.

The effect of pressure on all the metals tried, with the exception of antimony and bismuth, is to decrease the resistance. To a first approximation, the relation between pressure and resistance is linear. The average pressure coefficient is the datum which is of most immediate interest. The average coefficient up to 12000 kg. for any temperature was found by connecting the average zero with the average of the two maximum points (which in many cases were nearer 13000 than 12000 kg.) by a straight line, calculating and plotting the deviations of the observed points from this straight line, passing through these deviation points a smooth curve (one is shown for lead in Figure 2), and from this smooth deviation curve reading off the value of the deviation at 12000, which may then be combined with the slope of the straight line to give the average coefficient to 12000. The coefficient found in this way is called the "observed" average coefficient. "observed" coefficient is a function of temperature. The "observed" coefficient at each of the five temperatures was then plotted against temperature, a smooth curve drawn through the five points, and the value given by the smooth curve at any temperature taken as the best value of the coefficient for that temperature. In the following the smoothed average coefficient is given in tables as a function of temperature, and the experimental points are given in diagrams from which an estimate may be formed of the experimental accuracy.

To a second approximation the relation between pressure and resistance is not linear, but the initial rate of decrease of resistance is in all cases greater than that at higher pressures. The departure from linearity may vary with the substance from 0.8% to 5% of the total change of resistance under 12000 kg. For some substances

which depart little from linearity, the departure is symmetrical about the mean pressure, and may be represented within the limits of error by a second degree equation of the form Ap (12000—p). In these cases the manner of departure from linearity is entirely specified by giving the maximum departure. The initial slope of the pressure-resistance curve is the average slope plus four times the maximum percentage deviation, and the final slope is the average slope minus four times the maximum deviation. The departure from linearity is of course a function of temperature. The experimental values of the departure were plotted against temperature and smooth curves drawn through the points. In the tables the smoothed values of maximum departure are given as functions of temperature, and in a diagram the experimental values are given, from which the accuracy of the

departure from linearity may be estimated.

For most substances, however, the departure from linearity is not symmetrical, and the relation between pressure and change of resistance cannot be represented by a second degree equation. Furthermore, the manner of variation from linearity is different for different metals, so that it is not possible to represent the behavior of all metals by a formula containing only two constants. Lisell 2 and Beckman 6 found a two constant formula sufficient. Lisell's formula was a simple second degree expression,  $R = R_0(1 + \gamma p + \delta p^2)$ , and Beckman's was exponential,  $R = R_0 e^{ap+bp^2}$ . Any formula, however, must give correctly at least the average coefficient, the maximum deviation from linearity and the pressure of maximum deviation. At higher pressures all three of these data are unrelated, so that two constants will certainly not suffice. It might be possible to find a three constant formula which would work for all the metals within the limits of error, but I have preferred to exhibit graphically the deviations from linearity of each substance. The deviation curves are functions of temperature, so that to completely represent the data within my range a curve at each one of the five temperatures is necessary. The deviation curves have been smoothed as follows. First, smooth deviation curves were drawn through the experimental points at each temperature. The maximum deviation and the pressure of maximum deviation were next each plotted against temperature and smooth curves drawn through these points. These smoothed maximum deviations and pressures of maximum deviation are listed in the Tables, and the experimental values of maximum deviation are shown in the curves as functions of temperature. The smoothed deviation curves for each temperature were then further adjusted graphically so that the

maximum falls at the values indicated by the smooth curves. This adjustment of the maximum was always slight and could be made with little uncertainty. Finally, each one of these smoothed adjusted deviation curves was uniformly changed in scale by the factor necessary to make its maximum coincide with the maximum deviation found from the smoothed curves of maximum deviation against temperature, and these curves are given in the following as the "deviation curves."

It will conduce to clearness to give an example or two showing the combined use of the tables and the deviation curves. Let us find, for example, the resistance of tin at 5000 kg, and 50° in terms of its resistance at 0° and 0 kg.\* Turning to Table II, we find the average pressure coefficient at 50° is 0.05936 and the resistance at 0 kg. at 50° is 1.2179. If the relation between pressure and resistance were linear. the resistance at  $50^{\circ}$  would be  $1.2179 (1 - 5000 \times 0.05936) = 1.1609$ . But from the deviation curve, Figure 4, we find the deviation at 50°. and 5000 kg. to be 0.0046. The actual resistance at 50° and 5000 kg. is therefore 1.1609 - 0.0046 = 1.1563. Or let us find the initial pressure coefficient of lead at 75°. From Table V, the average coefficient at 75° is 0.041243. By drawing a tangent to the deviation curve, Figure 7, at 75° at the origin we find that the deviation for 1 kg. at 75° is 0.05302. But the initial resistance at 75° is 1.3127, so that the initial deviation at 75° for 1 kg. in terms of unit resistance at 75° is  $0.0_5302/1.3127 = 0.0_5230$ . Adding this to the average coefficient gives 0.041243 + 0.05230 = 0.041473 for the initial pressure coefficient of lead at 75°.

The column in the tables headed "coefficient at 12000 kg." requires a word of explanation, the meaning of "coefficient" not always being unambiguous. This means the instantaneous rate of change of resistance with pressure at the temperature in question divided by the resistance at 0 kg. at the temperature in question. In other words, it is the slope of the line plotting resistance against pressure, drawn to such a scale that the resistance at the temperature in question and 0 kg. is taken as unity. Later in this paper I shall discuss another "coefficient" as 12000 kg., this time "the instantaneous coefficient." By this will be meant the rate of change of resistance with pressure divided by the actual resistance at 12000 kg. and the temperature in question.

<sup>\*</sup>The pressures in the tables and diagrams are gauge pressures. To get absolute pressures, add approximately one kg. The difference between absolute and gauge pressure is in almost all cases far within the limits of error.

### DETAILED DATA.

The detailed data for individual substances follow. These are arranged in order of melting point, except for the anomalous substances bismuth, antimony, and tellurium.

Indium. A sample only one gram in amount was available from Merck, without analysis. This metal is as soft or softer than lead. It was extruded into a wire of 0.006 inch diameter in a die of special construction. Indium oxidizes much less rapidly than lead; after extrusion the surface of the wire is brightly polished and remains so for at least several weeks when exposed to the air. It was wound loosely on a bone core of the dimensions already given. Its actual resistance at 0° was 11.7 ohms. Connections were made by soft soldering with a miniature copper, using a fusible solder of melting point slightly above 100°. There is some difficulty in making a successful soldered connection because of the low melting point of the indium, which is about 155°. It alloys very rapidly with any ordinary solder, forming an alloy of much lower melting point than any of the constituents. It must be caught by the solder with a single well directed touch.

The melting point of the alloy at the soldered connections limited the range over which measurements could be made. Successful runs were made at 0°, 25°, and 50°, but at 75° the soldered connections dropped off. Difficulty because of alloying also made it necessary to omit the usual temperature seasoning; this in any event is not so necessary for a low melting metal as for a higher one. No irregularity to be ascribed to lack of seasoning was to be found. After the very first application of pressure to 12000 kg. at 0° there was a permanent change of zero of 1.3% of the total pressure effect. This may well have been a viscosity effect from the petroleum ether, since indium is the softest of all the substances tried and so is particularly susceptible. At 25° the permanent change of zero after 12000 kg. was only 0.3% of the pressure effect, and at 50° only 0.003%. The maximum deviation of any reading from the smooth curves is 0.3% of the total effect, and the average numerical deviation 0.13%.

The smoothed results are collected in Table I and the experimental points are shown in Figure 3. The average coefficient does not depart more than 0.2% from linearity with temperature. The deviation from linearity is not symmetrical about the mean pressure; it is so great that the initial slope is from 25 to 33% greater than the mean and the final slope from 12 to 16% less.

TABLE I.

INDIUM.

		Pre	ssure Coefficie	Maximum Deviation	Pressure	
Temp. °C.	Resistance	At 0 kg.	At 12000 kg.	Average 0-12000 kg.	from Linearity	Maximum Deviation
0°	1.0000	-0.041226	05891	041021	0058	5600
25	1.1002	1297	896	1051	70	5600
50	1.2015	1368	911	1081	83	5600

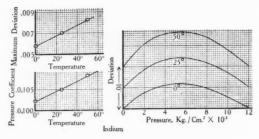


FIGURE 3. Indium, results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0°C. The pressure coefficient is the average coefficient between 0 and 12000 kg.

The average temperature coefficient found above, extrapolated for the range 0° to 100°, is 0.00407. This is considerably lower than the only other value I have been able to find, 0.00474 by Erhard.<sup>9</sup>

The general character of the results for indium is as follows. The average pressure coefficient of resistance increases linearly with temperature, but the increase is less than one third as much as the increase of resistance. The departure from linearity, on the other hand, increases at higher temperatures more rapidly than the initial resistance. This means that if resistance is plotted as ordinates against pressure for each of several temperatures and then if the scale of the

ordinates of the several curves is changed so as to make the resistance at 0 kg. independent of the temperature, the curves corresponding to the higher temperatures will drop off more sharply, and will also have greater curvature. This is entirely as one would expect, particularly if the curves are asymptotic to zero resistance at infinite pressure.

Tin. This was Kahlbaum's best, grade "K." It was extruded to 0.008 inch diameter and wound bare on a bone core. Its resistance at 0° and 1 kg. was 12.3 ohms. Connections were made by soldering with a fusible alloy of tin and lead of melting point about 180°. It was seasoned by heating to 120°, and by a preliminary application of 12000 kg. at 25°. Extrusion instead of drawing proved necessary. It was possible to draw the wire down to 0.01 inch, but there were many irregularities and it was not possible to wind it with silk insulation. Several unsuccessful preliminary attempts were made with the bare extruded wire on a hard rubber core. There were large initial irregularities due to the large thermal expansion of the hard rubber which entirely disappeared on using bone. With the final set-up the permanent change of zero after a run to 12000 was never more than 0.1% of the pressure effect, except at 0°, where the change jumped to 1%, probably because of viscosity of the transmitting medium.

Runs successful in every way were made at all five temperatures. The smoothed results are collected in Table II, and the experimental points are shown in Figure 4. Except for a single discordant point,

TABLE II.

TIN.

		Pr	essure Coefficie	nt	Maximum Deviation	Pressure
Temp. °C.	Resistance	At 0 kg.	At 12000 kg.	Average 0-12000 kg.	from Linearity	Maximum Deviation
0°	1.0000	041044	0₅833	0 <sub>5</sub> 9204	0036	5770
25	1.1080	1055	836	9280	415	5800
50	1.2179	1062	839	9357	47	5820
75	1.3306	1064	841	9434	525	5850
100	1.4473	1062	844	9510	58	5870

the maximum deviation of any point from the smoothed curves is 0.4% of the pressure effect, and the average numerical deviation is 0.07%, or, excluding the run at  $0^{\circ}$ , where the effect of viscosity was

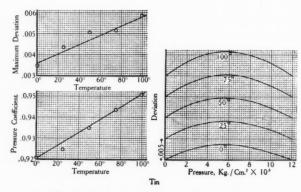


FIGURE 4. Tin, results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0° C. The pressure coefficient is the average coefficient between 0 and 12000 kg.

apparent, 0.03%. The deviation curves are sensibly not symmetrical, although the pressure of maximum deviation is very nearly the mean pressure.

The average temperature coefficient of tin between 0° and 100° was 0.00447. This is not quite as high as the value of Jaeger and Diesselhorst 8 for tin from the same source as this, which by their analysis had less than 0.03% lead. Their value for tin rod was 0.00459 (corrected for range as explained in the introduction).

The initial value of the pressure coefficient at  $0^{\circ}$  has been found by Beckman <sup>6</sup> to be  $-0.0_592$ . This is to be compared with  $-0.0_4104$  given above. The average coefficient to 12000 kg. agrees very closely with Beckman's value.

The general character of the results is the same as for indium. If the curves of resistance against pressure are so changed in scale that the resistance at 0 kg. for each temperature is the same, then the curves for the higher temperatures are the steeper and have the greater curvature.

Thallium. This was electrolytically prepared from two samples of metal which originally came from Merck and Eimer and Amend,

and was supposed to be chemically pure in its original state. The metal was first converted into the nitrate, and measurements made on the polymorphic transitions under pressure. From the nitrate it was converted to the iodide. These two conversions have been described in a previous paper.<sup>10</sup> The iodide was then converted to the sulfate by heating with c. p. sulfuric acid, and it was finally electrolyzed onto a platinum electrode from aqueous solution of the sulfate. After all these metamorphoses any impurity of the original metal should have been effectively removed. The purity of this electrolytic thallium was tested by comparing its temperature coefficient of resistance with untreated c. p. thallium from Merck. The mean coefficient at 0° from readings between 25° and 96° of electrolytic thallium was 0.005177 against 0.004898 of Merck's. The electrolytic is therefore appreciably

purer.

Thallium was formed into wire about 0.013 inch diameter by cold extrusion. It was wound loosely on a bone core and connections made by soldering with "fine" solder (2 parts tin to 1 part lead). Its initial resistance was 9.47 ohms at 0°. Thallium becomes coated rather rapidly in the air with brownish oxide. The layer of oxide in time becomes so deep as to very appreciably increase the resistance of the wire. There is also a slow formation of oxide on standing in the kerosene transmitting the pressure. The rate of formation of oxide is not great enough to introduce appreciable error during a single run; at 100° and 75°, where the rate of formation is most rapid, there was no perceptible permanent change of zero after the runs. When the apparatus stands over night, however, between runs, there is sufficient formation to introduce appreciable error into the temperature coefficient determined from successive zeroes. The runs at 25° and 0° were made 9 days after those at 50°, 75°, and 100°, and there was a break in the resistance of 5% in this interval due to oxidation. For this reason the relation between temperature and resistance has been taken as linear in the table and the value chosen for the mean coefficient is that found from the comparison of electrolytic with Merck's thallium.

The wire was seasoned before measurements by subjecting to 9000 kg, at  $95^{\circ}$  and 12000 at  $50^{\circ}$ .

The smoothed results are shown in Table III and the experimental values in Figure 5. The maximum deviation of any point from the smooth curve is 0.7% of the total pressure effect, and the average

<sup>10</sup> P. W. Bridgman, Proc. Amer. Acad. 51, 593 (1916), and 52, 151 (1916).

numerical deviation is 0.13%. The curves of deviation from linearity are not symmetrical about the mean pressure; these curves also are given in Figure 5.

There are no previous measurements of the pressure coefficient.

TABLE III.
THALLIUM.

		Pre	essure Coefficie	Maximum Deviation	Pressure	
Temp. °C.	Resistance	At 0 kg.	At. 12000 kg.	Average 0–12000 kg.	from Linearity	Maximum Deviation
0°	1.0000	041319	041017	041151	00580	5470
25	1.1292	1358	1023	1165	702	5530
50	1.2585	1393	1028	1183	823	5580
75	1.3877	1425	1028	1203	945	5640
100	1.5170	1456	1024	1226	1066	5700

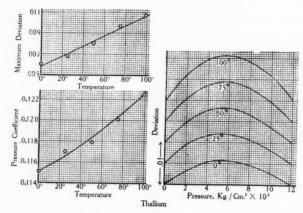


Figure 5. Thallium, results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0°C. The pressure coefficient is the average coefficient between 0 and 12000 kg.

For the temperature coefficient between 0° and 100° there are the values .00398 by Dewar and Fleming, 11 and .00458 by Matthiesen and Vogt. 12 These are both considerably lower than .00517, the value found above.

The general character of the results is the same as for indium and tin. When the resistance-pressure curves are plotted to the same initial scale, the curves for higher temperatures are steeper and have the greater curvature.

Cadmium. This material was from Kahlbaum, grade "K." It was made into wire by extruding when hot into a wire 0.06 inch diameter. The surface was then deeply etched to remove any possible impurity of iron introduced by the extrusion. From 0.06 inch it was drawn to the final size, 0.005 inch, through diamond dies and wound with one layer of silk insulation. The drawing and winding were done by the New England Electrical Works, Lisbon, N. H. It was seasoned after winding into the coreless toroid for pressure measurements by keeping

# TABLE IV.

		P	ressure Coefficie	Maximum Deviation	Pressure of	
Temp. °C.	Resistance	At 0 kg.	At. 12000 kg.	Average 0-12000 kg.	from Linearity	Maximum Deviation
0°	1.0000	041063	05746	058940	00567	5880
25	1.1012	1082	765	9104	604	5880
50	1.2057	1095	778	9212	640	5880
75	1.3133	1102	786	9257	676	5880
100	1.4240	1106	790	9270	713	5880

at 130° and 0° alternately for 30 minutes over a space of 8 hours and by 4 applications of 12000 kg. at 100°. Connection was made by soldering with "fine" solder. The resistance at 0° was 33.5 ohms. The smoothed results are shown in Table IV and the experimental

<sup>11</sup> J. Dewar and J. A. Fleming, Phil. Mag. 36, 271–299 (1893).
12 A. Matthiesen and C. Vogt, Phil. Mag. 26, 242 (1863).

points in Figure 6. Except for one point due to viscosity at 0°, the maximum departure of any reading from the smooth curve was 0.6% of the total pressure effect, and the average numerical departure, including every point, was 0.05%. A preliminary sample gave a few readings at  $75^{\circ}$  agreeing within the limits of sensitiveness with

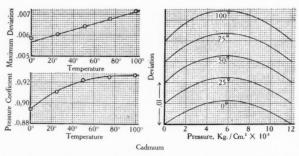


FIGURE 6. Cadmium, results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg. and  $0^{\circ}$ C. The pressure coefficient is the average coefficient between 0 and 12000 kg.

those finally obtained. Measurements on this preliminary sample were terminated by leak due to a defective cylinder. The deviations from linearity are very nearly, but not quite, symmetrical and parabolic. The deviation curves are also reproduced in Figure 6.

The average temperature coefficient between 0° and 100° at 0 kg. found above is 0.00424. This may be compared with values of Jaeger and Diesselhorst 8 for cadmium from the same source, showing by analysis less than 0.05% of Pb, Zn, or Fe. Their value for cadmium rod is .00421, and for wire 0.00396. (I have corrected both of their data by a factor of 1% to compensate for the difference of range.) The cadmium used above is therefore probably a little purer than that of Jaeger and Diesselhorst. Beckman 6a found 0.00425 for the average coefficient of the cadmium on which he made pressure measurements. The initial pressure coefficient at 0° has been found by Beckman to be -0.0592, against -0.041063 above. My average coefficient between 1 and 12000 kg. is -0.0594 and is in much better agreement with Beckman's initial value. Beckman found a variation of the coefficient of 1.7% over 2700 kg.

The general character of the results is somewhat different from those of the three previous metals. When the pressure-resistance curves are scaled to the same initial resistance, the curves for the higher temperatures are steeper, but are less curved.

Lead. I owe this material to the kindness of Mr. C. Wadsworth, who prepared it under the direction of Professor T. W. Richards in connection with determinations of the atomic weight of lead of ordinary and radio-active origin. It showed by spectroscopic analysis not more than 1 part in 300,000 of Ag and Cu, and no trace of any other metal. It was made into wire 0.013 inch diameter by cold extrusion, wound loosely on a bone core as usual, and connected to the leads with "fine" soft solder. Its initial resistance at 0° was 11.0 ohms. It was seasoned by preliminary applications of 12000 kg. at 50° and 100°.

TABLE V.

Temp. °C.	Resistance	Pi At 0 kg.	ressure Coefficie At. 12000 kg.	Maximum Deviation from Linearity	Pressure of Maximum Deviation	
0°	1.0000	041442	041044	041212	00660	5560
25	1.1022	1452	1045	1222	749	5590
50	1.2065	1462	1047	1232	838	5620
75	1.3127	1473	1049	1243	927	5650
100	1.4207	1483	1051	1253	1016	5690

The temperature coefficient of this excessively pure lead was compared with that of Kahlbaum's "K" lead, formed into wire of the same dimensions by extrusion in the same way. The coefficient of Kahlbaum's lead was 0.2% lower than this, thus again confirming this test of purity.

An unsuccessful attempt, terminated by a flaw in the cylinder, was made about two months before the successful runs. This first run was on Kahlbaum's "K" lead, drawn from 0.06 to 0.01 inch and silk insulated by the New England Electrical Works. It was very fragile, with many places of incipient break. One break was made in winding, and it had to be soft soldered in the center. A successful

run was made on this specimen at  $100^\circ$  before the cylinder broke; the average coefficient of this specimen at  $100^\circ$  was 0.5% lower than that of the pure specimen.

The smoothed results are collected in Table V and the experimental points are shown in Figure 7. The maximum departure of any single point from the smooth curve was 0.2% of the total pressure effect, and the average numerical departure was 0.026%. The deviation

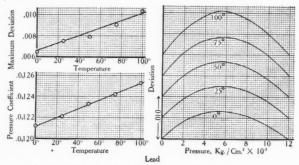


FIGURE 7. Lead, results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0°C. The pressure coefficient is the average coefficient between 0 and 12000 kg.

from linearity is very nearly symmetrical and parabolic, but there are distinct failures of symmetry in the usual direction. It is very noticeable at the higher temperatures that the curvature of the deviation curves is greatest near the maximum. This is unmistakably indicated by the data. The deviation curves are also given in Figure 7.

The temperature coefficient of the lead given in the table is 0.004207. The coefficient of a piece of the same lead, which had never been subjected to pressure, was found to be 0.00441. This value was found by extrapolation of the readings between 25° and 96°. It is this which is strictly comparable with the value 0.00428 of Jaeger and Diesselhorst <sup>8</sup> for Kahlbaum's "K" lead.

The initial pressure coefficient at  $0^{\circ}$  is given by Lisell  $^2$  as  $-0.0_4140$ . Williams  $^{13}$  found the relation between resistance and pressure to be linear over a range of 700 kg. and the value of the coefficient to be  $-0.0_4138$ . The value found above by graphical extrapolation from

the deviation curves is -0.04144. The agreement of these values is better than in the majority of cases.

The general character of the results is normal. When the resistance-pressure curves for the different temperatures are scaled to the same initial resistance, the curves for the higher temperatures are

steeper and are slightly more curved.

Zinc. This was Kahlbaum's grade "K." Spectroscopic analysis by Mr. A. E. Becker showed traces of cadmium, iron and lead. It was extruded hot into wire of 0.006 inch diameter and wound loosely on a bone core. Connections were made with ordinary soft solder. The initial resistance at  $0^{\circ}$  was 10.3 ohms. It was seasoned by several exposures to  $120^{\circ}$  at atmospheric pressure, and by three preliminary applications of 12000 kg. at  $100^{\circ}$ . A second sample of the same wire was used for the points at  $0^{\circ}$  and  $25^{\circ}$ . This was seasoned by subjecting to  $120^{\circ}$  and to 12000 kg. at room temperature.

The smoothed values are shown in Table VI and the experimental

TABLE VI.

ZINC.

		P	ressure Coeffici	ent	Maximum Deviation	Pressure
Temp. °C.	Resistance	At. 0 kg.	At 12000 kg.	Average 0-12000 kg.	from Linearity	Maximum Deviation
0°	1.0000	0 <sub>5</sub> 540	0 <sub>5</sub> 400	054700	00210	6000
25	1.1017	533	394	4634	231	6000
50	1.2050	529	389	4590	252	6000
75	1.3098	526	387	4562	273	6000
100	1.4159	524	385	4544	294	6000

values in Figure 8. The maximum departure of any point from a smooth curve was 0.9% of the total pressure effect, and the average numerical departure was 0.3%. These results are somewhat less regular than usual. Without making a bone core of new design it was not feasible to use a length great enough for the best results. Within the limits of error the deviations from linearity are symmetrical and parabolic.

The mean temperature coefficient of this wire, 0.00416, is distinctly higher than the best wire of Jaeger and Diesselhorst, for which they give 0.00402 (uncorrected for range). The zinc of Jaeger and Diesselhorst was from the same source as this and showed on analysis not more than 0.01% of Pb, Cd, or Fe. The initial pressure coefficient at 0° is given as  $-0.0_559$  by Lisell, against  $-0.0_5540$  found graphically from the deviation curve above. Lisell does not mention the source of his zinc, nor does he give its analysis or temperature coefficient. He did not regard it as one of his purer materials, and says that he estimates the error in his value to be not over 10%.

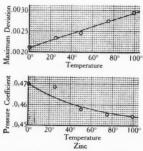


FIGURE 8. Zinc, results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0°C. The deviations are symmetrical about the mean pressure, so that it is not necessary to give the detailed deviation curves as in the preceding figures. The pressure coefficient is the average coefficient between 0 and 12000 kg.

The general character of the results is as follows. When the resistance-pressure curves for the different temperatures are scaled to the same initial resistance the curves at higher temperatures are *less* steep, but show very little difference of curvature.

Magnesium. The material available was commercial magnesium from Eimer and Amend, for which I have no analysis. It was extruded hot into wire 0.007 inch diameter and wound loosely on a bone core. The initial resistance was 5.6 ohms. It is a matter of great difficulty to make any sort of electrical connections; no commercial method is known. I was able to make a connection with aluminum solder which appeared good to the eye and gave satisfactory results up to 8000 kg. But beyond this the solder broke loose, probably because of unequal compression, and no further results of any constancy were possible. I also made indifferent connections with a

spring clip. The error in using the clip is introduced by the heavy coating of oxide, which forms rapidly on magnesium in the air, and has very high insulating qualities. With this clip a series of regular results were obtained between 12000 and 6000 kg., showing the same linear relation between pressure and resistance as the other run, but no other points of this run were at all good. It did not seem worth while to try for points at other temperatures than 0°. The pressure coefficient at 0° of this sample of magnesium may be taken to be  $-0.0_555$  within perhaps 1 or 2%. No attempt was made to find the deviations from linearity.

There are no previous measurements of the pressure coefficient over any range. For the temperature coefficient I found .00390 between 0° and 20°. This may be compared with 0.00381 between 0° and 100° by Dewar and Fleming.<sup>11</sup> The material was not very impure, evi-

dently.

Aluminum. This is one of most difficult of metals to get entirely pure. I obtained some considerably purer than that on which measurements are usually made through the courtesy of the Aluminum Company of America. Their analysis was Fe 0.23%, Si 0.24% Cu 0.06%, Al 99.47%. It was provided by them in the shape of ½ inch rod. I extruded it hot from this size to 0.06 inch diameter and etched the surface to remove iron. It was then drawn down to 0.005 inch through diamond dies and single covered with silk insulation by the New England Electrical Works. About 30 ft. of it was wound on itself into a coreless toroid and seasoned by carrying several times back and forth between 0° and 120° over an interval of 5 hours. Its initial resistance at 0° was 18.7 ohms.

Great trouble was found in making connections to this fine wire. Commercial aluminum solder was tried without success, the fine wire being completely alloyed through and eaten off at the temperature necessary to make a good connection. Finally connections were made with a spring clip but with results not entirely satisfactory. Consistent irregularities of as much as 4% of the total effect were found at the last three points with decreasing pressure at all temperatures, due probably to some slight slipping of the clip. The zero, however, was recovered satisfactorily; the permanent changes of zero were 1.4, 0.0, 0.6, 0.2, and 0.7% of the total effect. Except for the points a which consistent departures were found the greatest departure of any point from a smooth curve was 0.5% of the total effect. With a perfectly satisfactory method of making connections it might possibly pay to repeat these measurements searching for a polymorphic transition. The

possibility of such a transition with a very slight discontinuity of resistance is not entirely ruled out by these measurements, although it is exceedingly improbable.

TABLE VII.

#### ALUMINUM.

Temp. °C.	Resistance	P At 0 kg.	At. 12000 kg.	Average 0-12000 kg.	Maximum Deviation from Linearity	Pressure of Maximum Deviation
0°	1.0000	05416	05347	0 <sub>5</sub> 3815	00104	6000
25	1.1077	410	349	3794	101	6000
50	1.2159	405	351	3781	97	6000
75	1.3245	401	354	3772	93	6000
100	1.4337	397	356	3766	90	6000

The smoothed results are collected in Table VII, and the experimental values are shown in Figure 9. Within the limits of error the deviations from linearity are symmetrical and parabolic, and are sufficiently characterized by the values of the table.

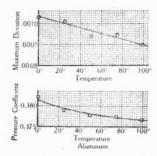


FIGURE 9. Aluminum, results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0°C. Since the deviations are symmetrical, there is no need for giving the detailed deviation curves. The pressure coefficient is the average coefficient between 0° and 12000 kg.

The mean temperature coefficient of the sample above was 0.00434, which is considerably higher than the best value of Jaeger and Diesselhorst,8 0.0039 (uncorrected). Their aluminum showed by analysis 0.5% Fe, and 0.4% Cu, and was therefore much less pure than the sample above. The initial pressure coefficient at  $0^{\circ}$  is given as  $-0.0_537$ by Williams <sup>13</sup> against -0.05416 from the deviation curves above. Williams does not give the analysis or temperature coefficient of his sample.

The results are somewhat unusual. When the resistance-pressure curves for different temperatures are scaled to the same initial resistance, the curves for the higher temperatures are very slightly less

steep, and very much less curved.

Silver. This was obtained in the form of wire 0.06 inch in diameter from the United States Mint at Philadelphia. The original material from which the wire was drawn was "proof" silver, in which no impurity whatever could be detected by any chemical test. The drawing was done with steel dies. After drawing, it was found that 0.03% of impurity had been introduced, which was probably mostly steel from the dies. I owe this examination of the effect of drawing to the interest and kindness of the late Dr. D. K. Tuttle. It seems safe to assume that the impurity so introduced was in the outer layers. I therefore removed the outer layers by scraping with glass, reducing the diameter from 0.06 to 0.04 inch. It is very probable that nearly if not all the 0.03\% of impurity was removed in this way, although I made no analysis of the wire after scraping. From the size 0.04 inch it was further drawn to 0.003 inch through diamond dies and wound with single silk insulation by the New England Electrical Works. It was annealed after the final drawing. For the pressure experiment it was wound on itself into a coreless toroid of 31.5 ohms resistance at 0°. It was seasoned in the same way and at the same time as the cadmium. Connections to the electrodes were made with silver solder.

The smoothed results are shown in Table VIII and the experimental points in Figure 10. The permanent change of zero after each run averaged 0.1% of the total effect; the maximum departure of any point from a smooth curve, except for one point at 0° where the viscosity was high, was 0.5%, and the average numerical departure was 0.1%. The departures from smoothness were almost entirely due to the viscosity of the kerosene used as a transmitting medium. This run was made before petroleum ether had been tried. The curves of deviation from linearity are not symmetrical or parabolic although

nearly so. They also are shown in Figure 10.

TABLE VIII.

SILVER.

		P	ressure Coefficie	Maximum Deviation	Pressure	
Temp. °C.	Resistance	At 0 kg.	At 12000 kg.	Average 0-12000 kg.	from Linearity	Maximum Deviation
0°	1.0000	0 <sub>5</sub> 308	05308	0₅3332	00088	5500
25	1.1011	363	311	3343	96	5660
50	1.2024	362	313	3352	995	5830
75	1.3044	359	315	3358	97	5990
100	1.4074	355	318	3362	905	6150

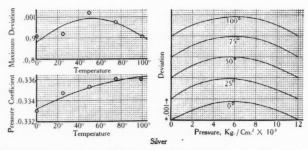


Figure 10. Silver, results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg. and  $0^{\circ}$ C. The pressure coefficient is the average coefficient between 0 and 12000 kg.

The average temperature coefficient between 0° and 100° was 0.00407, against 0.00400 found by Jaeger and Diesselhorst 8 for silver 99.98% pure. The initial pressure coefficient at 0° found from the deviation curve above was  $-0.0_5358$ , against  $-0.0_535$  by Lisell.² Lisell's silver was not excessively pure; it contained 0.08% of Cu and traces of carbon.

The results are somewhat unusual in general character. When the pressure-resistance curves of different temperatures are scaled to the same initial resistance, the steepness increases slightly at the higher temperatures as is normal, but the curvature becomes less at an accelerated rate as temperature increases. The shift of the pressure of maximum deviation from linearity to a value above the mean

pressure at the higher temperatures is also unusual.

Gold. The gold, like the silver, was furnished by the United States Mint at Philadelphia in the form of wire 0.06 inches in diameter drawn down through steel dies from bars of "proof" metal in which no impurity whatever could be detected chemically. Dr. Tuttle found that the amount of impurity introduced in the drawing was practically the same in amount as for the silver. I scraped the surface of this wire with glass, just as the silver, reducing the diameter to 0.04 inch. From this size it was drawn to 0.004 inch through diamond dies and covered with single silk by the New England Electrical Works. It was wound into a coreless toroid of 23.5 ohms initial resistance and seasoned at the same time as the cadmium. Connections were made by silver soldering.

The smoothed results are collected in Table IX, and the experi-

TABLE IX.

		P	ressure Coeffici	Maximum Deviation	Pressure	
Temp. °C.	Resistance	At 0 kg.	At 12000 kg.	Average 0-12000 kg.	from Linearity	Maximum Deviation
0°	1.0000	0 <sub>5</sub> 312	05276	0 <sub>5</sub> 2872	00062	4440
25	1.0977	310	275	2883	66	4910
50	1.1963	308	276	2895	665	5390
75	1.2960	306	279	2907	64	5860
100	1.3968	304	282	2918	59	6340

mental values of the average coefficient and maximum deviation from linearity in Figure 11. Kerosene was used as the transmitting medium throughout, and most of the departure from smooth curves is to be attributed to its viscosity. The average zero shift after a run was 0.16% of the total effect. Except for several points at  $0^\circ$ , where the viscosity is high, the maximum departure of any point from a smooth curve was 0.3% of the total effect, and the average numerical departure was 0.08%. The curves of deviation from linearity are distinctly not symmetrical, and show an unusually large progressive change in the location of the maximum with increasing temperature. The deviation curves are shown in Figure 11 also.

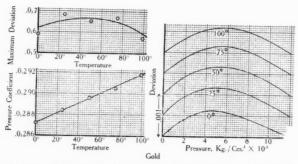


FIGURE 11. Gold, results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg, and 0°C. The pressure coefficient is the average coefficient between 0 and 12000 kg.

The average temperature coefficient between 0° and 100° listed above, 0.003968, is for the coil which had been subjected to pressure. Another coil of the same material, not subjected to pressure, gave 0.004009. The curves of resistance of each of these specimens against temperature were equally smooth, the departure from smoothness at any point not being more 1/7000 of the total change between 0° and 100°. It would seem, therefore, that 0.004009 should be taken as the best value for pure gold under normal conditions. This figure is to be compared with 0.00368 given by Jaeger and Diesselhorst 8 for "pure" gold. But the temperature coefficient of gold is unusually sensitive to impurity; Jaeger and Diesselhorst found that gold with 0.1% Fe, and 0.1% Cu and a trace of Ag had a coefficient of only 0.00203. Undoubtedly the lower value of Jaeger and Diesselhorst for "pure" gold is to be explained by slight impurities in their sample.

The initial pressure coefficient at  $0^{\circ}$  found graphically from the deviation curves above is -0.03117, which is to be compared with  $-0.0_527$  of Beckman.<sup>6</sup> He had trouble with change of zero in his measurements, and states that the error may be over 3%. The mean

temperature coefficient of Beckman's gold between  $0^{\circ}$  and  $100^{\circ}$  was 0.00390, nearly as high as the above.

The general character of the results is much the same as for silver. When the resistance-pressure curves are scaled to the same initial resistance, the curves at higher temperatures become slightly steeper but the curvature becomes less at an accelerated rate. There is also the same march toward higher pressures of the pressure of maximum

deviation, but here it is more pronounced than for silver.

Copper. I am indebted to the Bureau of Standards for this material; it was supplied from the stock of materials which had been used there in an extensive series of tests on the conductivity and temperature coefficient of copper from different sources. This was furnished by them in the form of wire 0.06 inch diameter. It had been forged from a bar of electrolytic copper without melting after the electrolytic refining. They were not in a position to supply the chemical analysis, but stated that it had proved to be of very high conductivity, and was in all probability purer than another sample which they offered me which showed by analysis 99.995% Cu, trace of S, and no Ag, Cu<sub>2</sub>0, As, Sb. From 0.06 inch I reduced the wire to 0.046 inch by etching nitric acid, to remove any contamination of iron introduced in the drawing. From this size it was drawn to 0.003 inch through diamond dies, annealed, and single silk covered by the New England Electrical Works. For the high pressure measurements it was wound into a coreless toroid and seasoned for temperature and pressure at the same time as cadmium. Its initial resistance at 0° was 35.5 ohms. Connections were made with silver solder.

The smoothed results are collected into Table X and the experimental values of average coefficient and maximum deviation from linearity are shown in Figure 12. This substance was one of the first investigated, before all the details of manipulation had been perfected. Pressure was transmitted by kerosene at all temperatures instead of by petroleum ether at 0° and 25°, so that the error from viscosity is larger than necessary. In spite of this, however, the maximum departure from a smooth curve, except the one most viscous point at 0°, was only 0.3% of the total effect, and the numerical average was 0.05%. The zero drift at  $75^{\circ}$  and  $100^{\circ}$  was larger than usual, amounting to 2%because the thermostatic control, which is more difficult at higher temperature, had not been perfected. At 50° the drift was 0.8%, at 25° 0.07%, and at 0° 0.00%. The curves of deviation from linearity are distinctly not symmetrical, and the pressure of maximum deviation progresses regularly with rising temperature. The curves are reproduced in Figure 12.

TABLE X.

COPPER.

		P	ressure Coeffici	Pressure Coefficient					
Temp. °C.	Resistance	At 0 kg.	At 12000 kg.	Average 0-12000 kg.	from Linearity	of Maximum Deviation			
0°	1.0000	0 <sub>5</sub> 201	05175	0 <sub>5</sub> 1832	00045	4200			
25	1.1073	196	174	1812	42	4650			
50	1.2146	192	173	1796	38	5100			
75	1.3219	188	172	1782	35	5550			
100	1.4293	184	171	1770	31	6000			

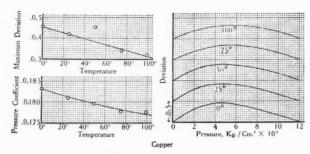


Figure 12. Copper, results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg. and  $0^{\circ}\mathrm{C}$ . The pressure coefficient is the average coefficient between 0 and 12000 kg.

A run at 25°, made with the same sample before the apparatus was running as regularly as finally, gave a mean coefficient to 12000 kg. 0.16% higher than that found in the final run.

The temperature coefficient listed in the table, 0.004293, was obtained from a coil of the same wire, subjected to the same seasoning but which had not been subjected to the pressure runs. There were somewhat large irregularities in the coil which was subjected to pressure runs.

sure. The value 0.004293 is a trifle higher than Jaeger and Diesselhorst's <sup>8</sup> highest value, 0.00428 for copper with less than 0.05% of Zn or Fe. The initial value of the pressure coefficient at 0°, found graphically from the deviation curves was  $-0.0_52008$ . This is to be compared with  $-0.0_5187$  of Lisell.<sup>2</sup> He does not give the temperature coefficient of his Cu, but states that chemical analysis showed no trace of any foreign metal. The difference in our values cannot be due to difference of thermal or mechanical treatment, because Lisell found no perceptible difference between the pressure coefficient of the same material when in the annealed or hard drawn state.

If the resistance-pressure curves are scaled to the same initial resistance, the curves for higher temperatures are less steep, and of much less curvature. There is the same abnormal march of the

pressure of maximum deviation shown by silver and gold.

Nickel. This was obtained from the Electrical Alloys Co. of Morristown, N. J., and was stated by them to be of high purity, although they gave no analysis. The purity was not as high as it should be, as will be seen later from the temperature coefficient. It was provided by them in the form of wire 0.003 inch diameter, double silk covered. For the measurements under pressure it was wound into a coreless toroid of 176 ohms resistance at 0°. The initial resistance was chosen so high because the pressure effect is very small. It was seasoned by many times heating and cooling between 0° and 140°, and by a single exposure to 12000 kg. at 25°. Connections were made with silver solder.

A few readings were made on another sample of nickel, kindly furnished by Leeds and Northrup. It is of the grade used by them in resistance thermometers, and is of high purity. It was probably not so pure as that used in the final readings, however, because its temperature coefficient was 3% lower. The results obtained with it are only of orienting value, because the temperature during annealing was accidentally allowed to get so high as to slightly discolor the silk insulation. At  $25^{\circ}$  the average pressure coefficient was 4% less than that of the purer sample.

The smoothed results are collected in Table XI and the experimental values of mean coefficient and deviation from linearity are shown in Figure 13. The results for nickel are not quite as regular as for many other metals, because the pressure coefficient is unusually small compared with the temperature coefficient. The zero drifts were not large, however, being respectively 1.1%, 0.16%, 0.2%, 0.1%, and 0.3% of the total pressure effect at 0°, 25°, 50°, 75°, and 100°.

The maximum departure of any point from a smooth curve was 0.6% of the total effect, and the average numerical departure was 0.15%.

TABLE XI.

NICKEL.

		P	Pressure Coefficient			Pressure
Temp. °C.	Resistance	At 0 kg.	At 12000 kg.	Average 0-12000 kg.	Deviation from Linearity	Maximum Deviation
0°	1.0000	0 <sub>5</sub> 1581	0₅1393	051473	000262	5240
25	1.1108	1578	1428	1498	242	5680
50	1.2288	1586	1464	1524	244	6020
75	1.3542	1600	1499	1549	263	6300
100	1.4873	1631	1535	1575	305	6540

The deviations from linearity are distinctly not symmetrical; they are also reproduced in Figure 13.

The average temperature coefficient between 0° and 100° was 0.00487. This would indicate a metal of fairly high commercial

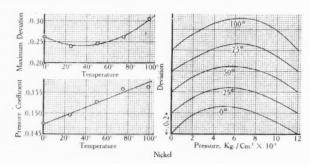


Figure 13. Nickel, results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0°C. The pressure coefficient is the average coefficient between 0 and 12000 kg.

purity, but not at all of the purity attainable by electrolytic means. Thus Jaeger and Diesselhorst  $^8$  give for their nickel, with an analysis of 97.0 Ni, 1.4 Co, 0.4 Fe, 1.0 Mn, 0.1 Cu, and 0.1 Si, 0.00438 as the temperature coefficient, but Fleming  $^{14}$  gives for electrolytic nickel 0.00618. It is probable that the temperature coefficient of nickel, like that of iron, is excessively sensitive to slight impurities. The initial value of the pressure coefficient at  $0^\circ$  as given graphically by the deviation curve was  $-0.0_5158$ , against  $-0.0_5138$  of Lisell $^2$ . Lisell does not give the temperature coefficient of his sample, but states that chemical analysis showed no trace of impurity.

The distinctive features of the behavior of nickel are shown when the pressure-resistance curves are scaled so that the initial resistances at different temperatures are the same. The curves at higher temperatures are steeper, but with less curvature, the rate of decrease of curvature being retarded at higher temperatures. The march of the pressure of the maximum is very pronounced. Too much significance should not be attached to any unusual features because of the lack of

perfect purity of this sample.

Cobalt. I owe this material to the kindness of Dr. Herbert T. Kalmus, who had prepared some samples of colbalt wire under the direction of the Canadian government. His analysis showed Co 98.71, Ni none, Fe 1.15, Si 0.14, Ca none, S 0.012, C 0.039, and P 0.010. The number of the sample which he sent me was H 214; under this number some of its other physical properties have been described in a publication of the Canadian government entitled "The Physical Properties of the Metal Cobalt". It was furnished in the form of wire 0.04 inch diameter. From this size it was most kindly swaged and drawn down to 0.003 inch under the direction of Dr. W. D. Coolidge of the General Electric Company. During the process of reduction it was annealed at 540°, and after its final reduction I further annealed it by heating to a cherry red for a few seconds in a muffler, exposed to the air. These elaborate processes were necessary because the wire cannot be drawn through dies like most metals. For the measurements under pressure it was wound bare on a bone core; at 0° its initial resistance was 71.9 ohms. Connections were made by silver soldering. After winding it was further seasoned by heating with the core to 135° for 2 hours. After the first application of pressure there was a permanent increase of resistance of 0.2% of the

<sup>14</sup> J. A. Fleming, Proc. Roy. Soc. 66, 50-58 (1899-1900).

total resistance, but after the first application of pressure the zero drift was no greater than for most substances.

Runs were made at only three temperatures, 0°, 50°, and 100°. I hoped at the time that a purer sample would be available and intended this run for orienting purposes, but the purer sample has not yet been successfully prepared.

The smoothed results are collected in Table XII, and the experimen-

TABLE XII.

#### COBALT.

Pressure Coefficient					Maximum Deviation	Pressure
Temp. °C	Resistance	At 0 kg.	At 12000 kg.	Average 0-12000 kg.	from Linearity	Maximum Deviation
0°	1.0000	06941	06805	06873	000204	6000
50	1.1825	845	755	860	161	6000
100	1.3651	755	697	726	118	6000

tal values of the mean coefficient and maximum departure from linearity in Figure 14. The pressure coefficient of cobalt is smaller than that of any other substance which I have found; one would, there-

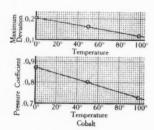


FIGURE 14. Cobalt, results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0°C. Since the deviations are symmetrical about the mean pressure, there is no need of giving the detailed deviation curves. The pressure coefficient is the average coefficient between 0 and 12000 kg.

fore, expect the results to be more irregular. The greatest departure of any point from the smooth curve is 0.8% of the total pressure effect and the numerical average is 0.35%. The deviation from linearity is symmetrical and parabolic within the limits of accuracy; there is no need of exhibiting the deviations graphically.

The mean temperature coefficient found above is 0.00365. Kaye and Laby give 0.0033. It is probable that this value is quoted from Reichardt<sup>15</sup>, who gives 0.00326 for cobalt 99.8% pure. There seem

to be no measurements of pressure coefficient for comparison.

A distinctive feature of the behavior of cobalt is the abnormally low pressure coefficient. When the resistance-pressure curves are scaled to the same initial resistance, the steepness is less by an unusual amount at the higher temperatures, as is also the curvature.

Iron. This material was American Ingot Iron, obtained from the American Rolling Mill Co. of Middletown, Ohio. It is of exceptional purity, showing less than 0.03% total impurity. Under microscopic analysis, done under the direction of Professor Sauveur, it appeared to consist entirely of ferrite. It is much purer than most samples which have been prepared in small amounts by the most refined methods in the laboratory. It was not furnished by the manufacturers in the form of wire, but this particular sample was provided in a sheet  $\frac{1}{16}$  inch thick. From this a square wire was cut with the shears, the corners rounded with the file, and it was drawn to 0.04 inch through It was then heavily etched and drawn to 0.005 inch through diamond dies and wound with single silk insulation by the New England Electrical Works. It was annealed by heating to redness after the final drawing. For the pressure measurements it was wound into a coreless toroid of 70 ohms resistance at 0°. Connections were made with silver solder. It was seasoned by heating repeatedly to 140°, and by several applications of 12000 kg.

The smoothed values are shown in Table XIII and the experimental values for mean coefficient and departure from linearity in Figure 15. The maximum zero drift was 0.03% of the total pressure effect. This was one of the earliest substances investigated, and pressure was transmitted at all temperatures by kerosene. The results are somewhat more irregular than usual. Except for four bad points, the maximum departure of any individual reading from a smooth curve was 0.54% of the total pressure effect, and the numerical average was 0.12%. Within the limits of error the deviation from linearity was

<sup>15</sup> G. Reichardt, Ann. Phys. 6, 832-855 (1901).

## TABLE XIII.

IRON.

		Pı	Pressure Coefficient			Pressure of
Temp. °C.	Resistance	At 0 kg.	At 12000 kg.	Average 0-12000 kg.	Deviation from Linearity	Maximum Deviation
0°	1.0000	052405	052119	0 <sub>5</sub> 2262	00043	6000
25	1.1416	2420	2150	2285	465	6000
50	1.2918	2436	2180	2308	495	6000
75	1.4519	2451	2209	2330	525	6000
100	1.6206	2468	2238	2353	56	6000

symmetrical and parabolic, and is therefore sufficiently characterized by the mean value in the table without graphical representation.

Iron was the first substance on which I made measurements, and many runs were made before the difficulties of temperature control were overcome, or the best methods of manipulation discovered. All the earlier results agreed within their larger limits of error with the final results.

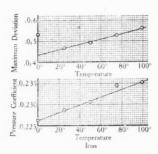


FIGURE 15. Iron, results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0°C. Since the deviations are symmetrical about the mean pressure, there is no need of giving the detailed curves. The pressure coefficient is the average coefficient between 0 and 12000 kg.

The mean temperature coefficient between 0° and 100° given above is 0.006206. This value was found from a coil of the same iron as that above, seasoned for temperature in the same way, but not subjected to pressure. The mean temperature coefficient of the coil used for pressure measurements was 0.006201. The agreement is unusually good, and shows very little internal change produced in this material by the application of pressure. I have adopted the value 0.006206 as more probably that of the pure metal in a state of complete ease. The unusually large departure of the relation between temperature and resistance from linearity is to be noticed. The value found above for the temperature coefficient of iron is exceptionally high, as is to be expected from its exceptional purity. Kaye and Laby give for pure iron 0.0062, essentially the same as the above. Dewar and Fleming <sup>11</sup> give 0.00625, for an iron said to be very pure, but without analysis. The large effect of impurity is to be inferred from data of Jaeger and Diesselhorst. who give for a sample composed of 99.55 Fe, 0.1 C, 0.2 Si, 0.1 Mn, trace of P, S, Cu, the value 0.00461, and for a purer iron with 0.1% C, other metals not determined, 0.00539.

The initial pressure coefficient at 0° has been found to be  $-0.0_{\circ}246$  by Beckman, 6 against  $0.0_{\circ}2405$  found graphically from the deviation curves above. The discrepancy is not as great as usual between our

results, and is in the opposite direction.

When the resistance-pressure curves are scaled to the same initial resistance at different temperatures the curves for higher temperature

become slightly steeper, but are less curved.

Palladium. This was furnished by Baker and Co. in the form of wire 0.04 inch diameter. It was not etched, but was from this size drawn down to 0.003 inch in diamond dies, annealed to redness, and single covered with silk by the New England Electrical Works. It was wound into a coreless toroid of 68.8 ohms resistance at 0°, and seasoned at the same time as the cadmium. Connections were made

by silver soldering.

The smoothed values ore collected in Table XIV, and the experimental values of mean coefficient and maximum deviation in Figure 16. The zero drifts during the runs were respectively 0.3%, 0.07%, 0.24%, 0.03%, and 0.9% of the total pressure effect at  $0^{\circ}$ ,  $25^{\circ}$ ,  $50^{\circ}$ ,  $75^{\circ}$ , and  $100^{\circ}$ . Pressure was transmitted at all temperatures by kerosene; it would be possible to increase the regularity of the results by using petroleum ether at  $0^{\circ}$  and  $25^{\circ}$ . The effect of viscosity seemed to be greater than usual. Except at  $0^{\circ}$ , the greatest departure of any single reading from a smooth curve was 0.2% of the total pressure

TABLE XIV.

#### PALLADIUM.

		Pressure Coefficient			Maximum Deviation	Pressure of	
Temp. °C.	Resistance	At 0 kg.	At. 12000 kg.	Average 0–12000 kg.	from Linearity	Maximum Deviation	
0°	1.0000	0 <sub>5</sub> 198	051855	0 <sub>5</sub> 1895	000215	5160	
25	1.0810	1965	184	1887	245	5430	
50	1.1609	1945	183	1879	24	5700	
75	1.2388	192	1825	1871	21	5970	
109	1.3178	1895	183	1863	16	6240	

effect, and the average numerical departure was 0.075%. At 0° the maximum departure was 0.7%, and the numerical average 0.31%. The deviation from linearity is not parabolic or symmetrical; the curves are shown in Figure 16.

The average temperature coefficient listed above is 0.003178 between 0° and 100°. This was obtained from a coil of the same sort as that on which the pressure measurements were made, subjected to the same seasoning, but used as the comparison coil of the Carey Foster

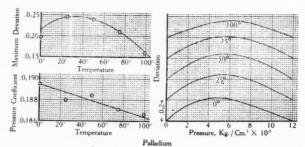


Figure 16. Palladium, results for the measured resistance. The deviation from linearity are given as fractions of the resistance at 0kg, and 0°C. The pressure coefficient is the average coefficient between 0 and 12000 kg.

bridge in the bath external to the cylinder. The coil on which the pressure measurements were made showed essentially the same value, 0.003175, but the results were a trifle less regular. The abnormal deviation of the resistance of palladium from linearity with the temperature is to be noticed; the slope of the resistance-temperature curve is greater at 0° than at 100°. This behavior is also shown by platinum, but is the opposite of that of all the other metals previously listed in this paper. This palladium cannot be very pure, because its temperature coefficient is low. Kaye and Laby give 0.0037, and Waidner and Burgess from the Bureau of Standards give .00333 to .00337. The latter value is probably as good as that of Kaye and Laby.

For the initial pressure coefficient at 0° Beckman <sup>6</sup> gives 0.0<sub>5</sub>219 against 0.0<sub>5</sub>1983 found graphically from the deviation curves above. Beckman does not give the temperature coefficient of his palladium.

When the resistance-pressure curves are scaled to the same initial resistance, the curves at higher temperatures are less steep. At first the curvature becomes greater with increasing temperature but

passes through a maximum and becomes rapidly less.

Platinum. This was the best Heraeus platinum, used in thermometry. I am indebted for it to Professor H. N. Davis, who before letting me use it had made a number of measurements on its temperature coefficient. The wire was wound bare on a bone core, was of 0.0038 inch diameter, and had an initial resistance at 0° of 21 ohms. It would have been better if I had been able to obtain a longer piece, but all the usual sources of supply were closed, and I was fortunate to obtain this. It had been annealed to a red heat a number of times by Professor Davis; after winding on the bone core it was still further annealed by carrying back and forth between 20° and 130° a number of times over an interval of four hours. It was seasoned for pressure by one application of 12000 kg. at 0°; a decrease of resistance of 2% of the total pressure effect was produced by the preliminary application. It was soldered with ordinary soft solder to copper leads.

The smoothed results are collected in Table XV, and the observed values of mean coefficient and deviation from linearity are shown in Figure 17. Because of the too low resistance the results are more irregular than usual. There was an unexplained systematic discrepancy, amounting to not more than 3%, at the maximum pressure at 0°, 25°, and 50°. Except for these irregularities at the maximum the greatest departure of any single point from a smooth curve was 0.5% of the pressure effect, and the average numerial departure was 0.14%.

Within the limits of error the departure from linearity is parabolic and symmetrical, and is sufficiently characterized by the numerical values in Table XV.

The mean coefficient between 0° and 100° listed above, 0.003868,

TABLE XV.

PLATINUM.

	١.	Pressure Coefficient			Maximum Deviation	Pressure	
Temp. °C.	Resistance	At. 0 kg.	At 12000 kg.	Average 0-12000 kg.	from Linearity	Maximum Deviation	
0°	1.0000	0 <sub>5</sub> 1975	0 <sub>5</sub> 1765	0 <sub>5</sub> 1870	000315	6000	
25	1.0967	195	1771	1862	30	6000	
50	1.1934	1935	1774	1854	283	6000	
75	1.2901	1915	1776	1846	27	6000	
100	1.3868	190	1777	1838	255	6000	

was obtained during the pressure measurements. This was somewhat lower than the value found by Professor Davis for the same piece, 0.003905, before it had been subjected to pressure. His value is high and indicates the highest purity. The same abnormal deviation from linearity with temperature was found as for palladium. The deviation was too small to be sure of quantitatively, and in the table the relation is given as linear.

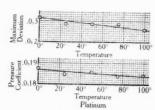


FIGURE 17. Platinum, results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0°C. The pressure coefficient is the average coefficient between 0 and 12000 kg.

For the initial pressure coefficient at 0° the above deviation curves give by graphical construction  $-0.0_5198$ , against  $-0.0_5177$  found by Lisell.<sup>2</sup> He does not give the temperature coefficient of his platinum, but chemical analysis showed an impurity of 0.28% iridium. We will see later that the discrepancy is very probably due to impurity. Lafay <sup>3</sup> gives for "pure" platinum the pressure coefficient  $0.0_5186$ ; he found the relation between pressure and resistance linear up to  $4000~\mathrm{kg}$ .

Before this run with Heraeus platinum, a complete series of runs was made with a specimen from Baker and Co., their purest. was subjected to preliminary treatment in all details like that of palladium, and the results were of the same regularity as those for palladium. The pressure coefficient was found to decrease linearly with temperature from 0.051766 at  $0^{\circ}$  to 0.051742 at  $100^{\circ}$ . The deviation curves were not symmetrical, and have the same distinct progression with temperature of the pressure of maximum deviation as have those of nickel. But a low value for the mean temperature coefficient was found, 0.003466, showing distinctly large impurities. It is to be noticed that the initial pressure coefficient at 0° is almost exactly the same as that found by Lisell. This makes it almost certain that the lowness of his pressure coefficient is due to the 0.28% of iridium. The fact that the deviation curves for impure platinum show a marked progression of the maximum, whereas those of pure platinum do not, suggests that the progression of the maximum found for nickel may be a spurious effect due to impurity.

The general character of the results is exactly the reverse of what we should be tempted to call normal. If the resistance-pressure curves are scaled to the same initial resistance for all temperatures, the slope

and curvature are both less at higher temperatures.

Molybdenum. This was obtained from the General Electric Co. through the kindness of Dr. W. D. Coolidge. It was in the form of bare wire 0.0011 inch diameter. It was seasoned by a number of excursions between 0° and 130°, and was then wound bare on a bone core. The resistance at 0° was 83.8 ohms. Some little trouble was found in making a suitable connection; silver solder will not stick to it. It may be readily attached to platinum by arcing in hydrogen, which is the method employed by the General Electric Co. But this does not make a perfectly sharp contact, there being a small region of imperfect contact where the fine molybdenum wire leaves tangentially the surface of the larger platinum wire. It is very difficult to make a butt joint without the use of special devices. It seemed to me

that this region of imperfect contact was an undesirable feature, because it might give rise to slight changes of resistance under pressure. Very good connections were finally made by using pure gold as a solder. A wire of platinum and molybdenum were laid side by side and wrapped with pure gold wire, 0.004 inch diameter. By arcing in hydrogen from a graphite point to the end of the wire the gold melts and runs back over the surface, wetting both platinum and molybdenum, and making a very good contact.

Before the final runs on molybdenum, a complete set of runs was made with the molybdenum wound on a core of hard rubber instead of bone. There were large initial irregularities due to the expansion of the rubber, which disappeared above 1000 kg. Between 1000 and 12000 kg. the results of the first run agreed within the limits of error with those of the final runs.

The smoothed results are collected in Table XVI and the experi-

TABLE XVI.
MOLYBDENUM.

		Pressure Coefficient			Maximum Deviation	Pressure	
Temp. °C.	Resistance	At 0 kg.	At. 12000 kg.	Average 0-12000 kg.	from Linearity	Maximum Deviation	
0°	1.0000	0 <sub>5</sub> 133	051245	051286	000124	6000	
25	1.1071	132	124	1281	128	6000	
50	1.2150	131	124	1275	132	6000	
75	1.3238	1305	1235	1270	136	6000	
100	1.4336	130	123	1265	140	6000	

mental values of mean coefficient and deviation from linearity in Figure 18. With the exception of three bad points at  $100^{\circ}$ , the largest departure of any single point from the smooth curve was 0.4% of the total pressure effect, and the average numerical departure was 0.075%. The deviations from linearity are within the limits of error symmetrical and parabolic; there is no need for graphical representation.

The average temperature coefficient between 0° and 100° is 0.004336. This is to be compared with the value 0.0034 given by Somerville, <sup>16</sup> In the tables of Kaye and Laby, the value is given as 0.0050, with no

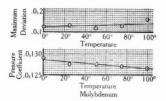


FIGURE 18. Molybdenum, results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0°C. Since the deviations are symmetrical about the mean pressure, there is no need of giving the detailed curves. The pressure coefficient is the average coefficient between 0 and 12000 kg.

reference except the year 1910. Since I have been able to find no other reference for the temperature coefficient of molybdenum, and the work of Somerville was published in 1910, it seems plausible to suppose the value of Kaye and Laby is a misprint. The amount of impurity in my specimen was stated by Dr. Coolidge to be of the order of 0.2%. There are no previous measurements of the pressure coefficient for comparison over any range.

When the resistance-pressure curves are scaled to the same initial resistance for all temperatures the curves for higher temperatures are

found less steep and less curved. This is like platinum.

Tantalum. This was obtained from the General Electric Co. through the kindness of Mr. MacKay. It is bare, 0.0022 inch diameter. It was subjected to the same seasoning as the molybdenum, and was wound bare on a core of bone with an initial resistance at 0° of 82.1 ohms. A perfectly satisfactory method of connection was not found. Neither gold nor silver solder will stick to the surface. Connection may be made to platinum by arcing in hydrogen, but the tantalum becomes excessively brittle in places where it has been subjected to a high heat, and the connection is very likely to drop off. Connection was finally made with a simple spring clip, consisting of a tightly wound helix of small piano wire. The spring is stretched, and the tantalum wire dropped between the extended spires. The results

<sup>16</sup> A. A. Somerville, Phys. Rev. 31, 261-277 (1910).

are somewhat more irregular than usual, but no consistent error seems introduced by this sort of a connection.

The smoothed results are shown in Table XVII, and the experi-

## TABLE XVII.

TANTALUM.

		Pr	essure Coefficie	Maximum Deviation	Pressure	
Temp. °C.	Resistance	At 0 kg.	At 12000 kg.	Average 0-12000 kg.	from Linearity	Maximum Deviation
0°	1.0000	0 <sub>5</sub> 1487	051373	0 <sub>5</sub> 1430	00017	6000
25	1.0743	1497	1391	1444	17	6000
50	1.1486	1507	1409	1458	17	6000
75	1.2229	1518	1426	1472	17	6000
100	1.2973	1530	1442	1486	17	6000

mental values of mean coefficient and deviation from linearity in Figure 19. The zero creep during a run amounted on one occasion to as much as 2% of the total effect, but was otherwise less than 1%. The maximum departure of any single point from a smooth curve was 0.5% of the total effect, and the average departure was 0.1%.

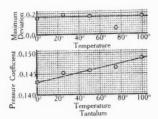


FIGURE 19. Tantalum, results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg. and 0°C. Since the deviations are symmetrical about the mean pressure, there is no need of giving the detailed curves. The pressure coefficient is the average coefficient between 0 and 12000 kg.

Within the limits of error the deviation from linearity is symmetrical and parabolic; the numerical values are given in Table XVII.

The temperature coefficient found above between 0° and 100° was 0.00297. Kaye and Laby give 0.0033, evidently taken from W. von Bolton. On consulting the original paper, 17 however, it will be found that the value is given with only one significant figure, 0.003. The agreement of our results is, therefore, within the limits of error. The General Electric Co. was not able to give any information about the purity apart from that afforded by the temperature coefficient.

There seem to be no previous measurements of the pressure coeffi-

cient for comparison.

When scaled to the same initial resistance, the resistance-pressure curves are found to be steeper at the higher temperatures, but less curved.

Tungsten. This was obtained from the General Electric Co. through the kindness of Dr. W. D. Coolidge. It is bare and 0.0004 inch diameter. It was seasoned for temperature at the same time as Mo and Ta and for pressure by a single application of 12000 kg. at 0°. There was no perceptible change of zero after the very first application of pressure. It was wound loosely in two or three turns on a smooth bone cylinder, and held loosely in place with silk thread. Its initial resistance at 0° was 79.0 ohms. Connections were made with gold

solder to platinum by arcing in hydrogen.

The smoothed results are collected in Table XVIII, and the experimental values of mean coefficient and departure from linearity are shown in Figure 20. The zero drift during a run was not large, being respectively 0.25%, 0.0%, 0.56%, 0.08%, and 0.054% of the total effects at 0°, 25°, 50°, 75°, and 100°. The individual results were irregular, however. At 75° and 100° in particular, there are large irregularities in a direction opposite from that of hysteresis. The maximum departure of any point from a smooth curve was 0.7% of the total effect, and the numerical average 0.15%. The deviation from linearity is slight; within the limits of error it is symmetrical and parabolic. The characteristic numerical values are given in Table XVIII.

The average temperature coefficient found above is 0.00322. This is low compared with the value 0.0050 of Somerville. He found a rather unusually large departure from linearity with temperature. The source of Somerville's tungsten was the same as mine, the General

<sup>17</sup> W. von Bolton, ZS. Elektrochem. 11, 45 (1905).

TABLE XVIII.

TUNGSTEN.

		Pi	ressure Coefficie	Maximum Deviation	Pressure	
Temp. °C.	Resistance	At 0 kg.	At 12000 kg.	Average 0-12000 kg.	from Linearity	Maximum Deviation
0°	1.0000	0 <sub>5</sub> 1279	0 <sub>5</sub> 1189	0 <sub>5</sub> 1234	000135	6000
25	1.0795	1283	1197	1240	14	6000
50	1.1595	1288	1204	1246	145	6000
75	1.2402	1292	1212	1252	15	6000
100	1.3219	1297	1219	1258	155	6000

Electric Co., but his sample was obtained in 1910. There would seem to be no reason to suspect the purity of his sample to be greater than mine. Dr. Coolidge says that the impurity is of the order of 0.2%.

There seem to be no previous measurements of the pressure coefficient for comparison.

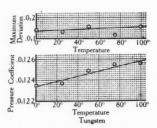


FIGURE 20. Tungsten, results for the measured resistance. The deviations from linearity are given as fractions of the resistance at 0 kg, and 0°C. Since the deviations are symmetrical about the mean pressure, there is no need for giving the detailed curves. The pressure coefficient is the average coefficient between 0 and 12000 kg.

The general behavior is like that of Tantalum. When scaled to the same initial resistance, the resistance-pressure curves become steeper at the higher temperatures, but have less curvature.

Antimony. This was obtained from Eimer and Amend. They were so kind as to make a special analysis for me; this showed Sb 99.45%, As trace, Fe trace, other foreign metals none. It was formed into wire 0.013 inch diameter by hot extrusion. It is necessary to heat to 350° or 400° C, and apply a pressure of 10000 or 15000 kg. A little trick is necessary to successfully extrude it; this matter is described at length in a forthcoming number of The Physical Review. The wire is excessively brittle. It cannot be wound into any sort of a spiral, but must be used in straight lengths, in a sort of grid. The grid used was composed of two pieces laid together in the form of a V in grooves cut on a bone cylinder, attached together by soldering with "fine" solder at the bottom of the V. Connections to the leads was made by soft soldering at the top to flexible copper conductors made of many strands of wire 0.002 inch diameter. The soldering must be performed by a rapid touch, because the fine wire alloys very rapidly to form an alloy of much lower melting point than the solder applied. The initial resistance at 0° was 0.90 ohms. The sensitiveness is not as great as would have been desirable, but the difficulties of manipulation in making a larger grid would have been

Six runs were successfully made, at  $0^{\circ}$ ,  $25^{\circ}$ ,  $50^{\circ}$ ,  $75^{\circ}$ ,  $100^{\circ}$ , and at  $0^{\circ}$  again. It was a great gratification that such high pressures could be applied without rupturing this excessively brittle substance. At the low temperatures pressure was transmitted by petroleum ether, and at higher temperatures by kerosene. The behavior of antimony is abnormal, like that of bismuth, since it has a large positive pressure coefficient. There is rather large hysteresis, but within the limits of error the mean of points with increasing and decreasing pressure are linear. At  $0^{\circ}$  there was a permanent increase of resistance of 5% of the total resistance after the first application of pressure. After the first application of pressure the permanent changes of resistance

remained much smaller.

The smoothed results are shown in Table XIX, and the experimental values of the mean coefficient in Figure 21. The change of pressure

coefficient with temperature is abnormally large.

The temperature coefficient of this antimony wire between 0° and 100° was 0.00473. This may be compared with the value 0.00418 for cast antimony given by Matthiesen and von Bose. 18 Doubtless part of the difference at least can be ascribed to difference of mechanical treatment.

<sup>18</sup> A. Matthiesen und M. von Bose, Pogg. Ann. 115, 353-396 (1862).

TABLE XIX.

ANTIMONY.

Range 12000 kg.

Temperature	Resistance at 0 kg.	Average Pressure Coefficient
0°	1.000	+.041220
25	1.113	1107
50	1.229	994
75	1.349	881
100	1.473	768

There are no previous measurements of the pressure coefficient. The temperature measurements were continued from 100° to 170°, because a polymorphic transition has been suspected above 100°. In fact I did find a discontinuity in resistance at about 145°, thus verifying the approximate location of a transition as found by Jaenecke. 19

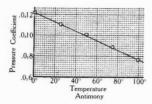


Figure 21. Antimony, the pressure coefficient at different temperatures. The coefficient is constant between 0 and  $12000~\rm kg$ .

No trace of the transition was found at any pressure in the temperature range of the measurements above, however, and the results are unaffected by the existence of the transition. The study of this transition is a separate question which must be taken up later. It must first of all be established that it is a true polymorphic transition in the sense that the crystals pass from one crystalline system to another.

Tellurium. I owe this to the kindness of Professor G. W. Pierce, who obtained it from Mr. Samuel Wien of New York City. Beyond the statement that it had been especially refined by Mr. Wien, I have no direct knowledge of its purity. It was formed into wire 0.013 inch diameter by hot extrusion. When the right temperature has been found by trial, pieces one or two feet long may be obtained. Like antimony it is excessively brittle, and must be used in the shape of a

grid of straight pieces.

Tellurium is only semi-metallic in its properties, and can not be soldered in the ordinary way. When fused it will stick to platinum, however. Connections were made by fusing to fine platinum wire. The end of the tellurium wire was allowed to rest by its own weight on a piece of fine platinum, and current was passed through the platinum sufficient to melt the tellurium and flow it over the surface. This connection was not entirely satisfactory, however, but apparently cracked above 10000 kg. because of the unequal compressibility of tellurium and platinum. There was a very large permanent increase of resistance after the run.

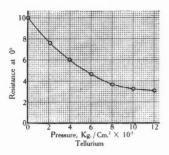


FIGURE 22. Tellurium, resistance as a function of pressure at 0°C. This curve was obtained with increasing pressure; on releasing pressure the curve is not retraced, and there is a large permanent increase of resistance.

Only one run was made on tellurium, at 0°. The points with increasing pressure were regular, and are shown in Figure 22. The resistance decreases under pressure, and the decrease is abnormally large, initially ten times more rapid than that of lead.

All of the electrical properties of tellurium are unusual, and are very variable; it is seldom that two observers obtain the same numerical value for any of its properties. The explanation for this seems to be that tellurium under ordinary conditions contains two modifications in unstable equilibrium, and the proportions of the two varieties changes greatly with the manner of treatment. The temperature coefficient of the same piece may be positive or negative according to the thermal treatment. The pressure coefficient of tellurium has been very recently measured by Beckman  $^6$  who used small rods of tellurium cast in glass. His specimens were subjected to various thermal treatments, and it was possible to find a connection between the pressure coefficient and the manner of treatment. The specific resistance of his samples varied from 0.0493 to 0.617 ohms per cm. cube. The pressure coefficient varied linearly with the resistance from  $-9.1 \times 10^{-5}$ . to  $-26.6 \times 10^{-5}$ .

The specific resistance of the specimen used above was much lower than any found by Beckman, being only 0.00645 ohms per cm. cube. The initial pressure coefficient was -0.00012, which is included in Beckmann's range. The average temperature coefficient between 24° and 0° was -0.0063. This is larger numerically than any of the negative coefficients found by Beckman. It is evident therefore, that the properties of the extruded metal are quite different from those of the cast metal.

Bismuth. Runs were made on three different samples of varying purity. It is known that the specific resistance and temperature coefficient of bismuth are very sensitive to small impurities; a fraction of a per cent of lead or tin may change the temperature coefficient from positive to negative and increase the specific resistance several fold. Minute impurities also introduce complicated hysteresis effects. The samples used in this work were Kahlbaum's ordinary grade, Kahlbaum's "K" grade, and electrolytic bismuth of my own preparation. The purification of bismuth is a matter of some difficulty; it is known that no chemical method will suffice. I used the method of electrolysis from the solution of the fluo-silicate described by Foerster and Schwabe.<sup>20</sup> It is essential to keep the current density low and to continually stir the bath.

The wire, which was 0.013 inch in diameter, was formed in each case by extrusion when warm. It was wound loosely on a bone core and connected to the leads with "fine" soft solder. At 100° the purest

<sup>20</sup> F. Foerster und E. Schwabe, ZS. Elektrochem. 16, 279 (1910).

sample alloyed with the solder and the leads dropped off, so that the run at 100° was not made; the connections to the two impurer samples were undamaged at 100°. The initial resistances at 0° were 3.8, 4.0, and 6.9 ohms respectively with decreasing purity; the lengths of the wires were in all cases about the same.

The effect of pressure on bismuth is abnormal, as it is for antimony, the pressure coefficient being large and positive instead of negative as usual. The positive coefficient was shown by all three samples. The most marked effect of impurity is that after a cycle of changes of temperature or pressure resistance does not return to its original value. Furthermore, the runs at constant temperature show great pressure hysteresis; this hysteresis becomes less as the impurity decreases. At 0° the most impure specimen showed a hysteresis of 12% of the total effect, and a permanent change of resistance after the run of 8% of the effect. The hysteresis is without doubt due to internal viscosity, which prevents the constitution of the mixed crystals keeping exact pace with the changes of pressure. This is suggested strongly by the fact that after every change of pressure an abnormally long time elapsed before the resistance became approximately constant. This view is also consistent with the observation that at higher temperatures the hysteresis rapidly became less. On making a run at 0° again after the run at 100° the original hysteresis had returned to almost its original value; the decreasing hysteresis at higher temperatures cannot, therefore, be an effect of accommodation. The average pressure coefficient between 0 and 12000 kg. decreased from +0.04281 at 0° to +0.04201 at 100°. The sample of grade "K" showed much less hysteresis, and did not require an appreciably longer time than any other metal to reach equilibrium after a change of pressure. The maximum permanent change of zero was 4% of the pressure effect at 0°, and the maximum hysteresis was also at 0° and was 3.5% of the total effect. The average pressure coefficient between 0 and 12000 kg. decreased from +0.04269 at  $0^{\circ}$  to +0.04205 at  $100^{\circ}$ .

The electrolytic bismuth was seasoned before the runs by several excursions between  $0^{\circ}$  and  $130^{\circ}$  at atmospheric pressure and by one application of 12000 kg. at  $0^{\circ}$ . It showed no peculiarity of behavior suggesting impurity except a hysteresis amounting at the most to 3% of the total effect at  $0^{\circ}$ . The permanent change of zero after a run was not over 0.3% of the total effect, which is not larger than found for several other metals, and no longer time was required for the attainment of steady conditions than was necessary for dissipation of the heat of compression. The curves of actual resistance against pressure

are shown in Figure 23 at 0°, 25°, 50°, and 75°, and the numerical values of resistance are given in Table XX. It has already been mentioned that the run at 100° was omitted because the solder alloyed with the bismuth and melted it off. The resistance curves are convex toward the pressure axis; furthermore the steepness increases with pressure faster than the resistance itself, so that the instantaneous

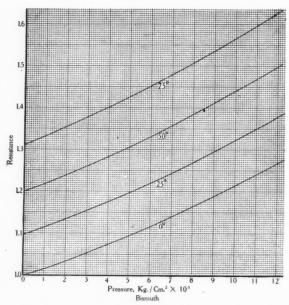


FIGURE 23. Bismuth, resistance as a function of pressure at several temperatures.

pressure coefficient increases also with pressure. The same abnormal curvature was shown by the two impurer samples. The numerical values of the average and instantaneous coefficients are shown in Table XXI. The behavior here is exactly the reverse of that of normal metals, for which the pressure coefficient becomes numerically less at higher pressures. The experimental values of the average coefficient to 12000 kg, are shown in Figure 24.

TABLE XX.

RESISTANCE OF BISMUTH.

Pressure		Resis	stance	
kg/cm <sup>2</sup>	0°	25°	50°	75°
0	1.0000	1.0969	1.1996	1.3115
2000	1.0336	1.1333	1.2389	1.3540
4000	1.0726	1.1748	1.2830	1.4013
6000	1.1163	1.2204	1.3316	1.4527
8000	1.1638	1.2698	1.3841	1.5078
10000	1.2143	1.3225	1.4498	1.5664
12000	1.2672	1.3779	1.4980	1.6279

It is evident from a comparison of the data for the different grades of bismuth that the effect of impurity on the temperature coefficient is much greater than on the pressure coefficient. The temperature coefficient of the impurest bismuth above was on the average negative (= -0.00039) over the range 0° to 100°; its resistance passed through a minimum at 75°. The coefficient of grade "K" was 0.00332 between 0° and 100°, and the instantaneous coefficient at 0°, was about 0.0027. The average temperature coefficient of the electrolytic bismuth above may be found from an extrapolation of the data of Table XX to be 0.00438, and the instantaneous coefficient at 0° 0.00381. Another sample from the same piece of wire, which had not been subjected to pressure at all, gave 0.00441 between 0° and 100°, and 0.00389 at 0°. These latter values may be accepted as more probably correct for this material in a state of ease.

The mean temperature coefficient of pure bismuth between 0° and 100° is given by Jaeger and Diesselhorst 8 as 0.00454, but as already explained, their value was obtained by an extrapolation, assuming linearity. If we assume that their deviation from linearity was the same as that found above, their temperature coefficient between 0° and 100° corrects to 0.00438, slightly less than the best value above.

TABLE XXI. PRESSURE COEFFICIENT OF BISMUTH.

		Pressure	Coefficient	
Temp.	Average 0-12000 kg.	Instan 0 kg.	taneous Coefficien	t 12000 kg.
0°	+.042227	+.04153	+.04195	+.04212
25	2142	155	.198	206
50	2076	155	192	199
75	2023	154	185	194

Other values for the temperature coefficient between 0° and 100° are 0.00429 by v. Aubel,<sup>21</sup> and 0.00458 by Lenard,<sup>22</sup> This last is considerably higher than any of the above. It is, however, difficult to estimate the accuracy which Lenard and v. Aubel ascribed to their own measurements. Lenard and Howard 23 give without comment as

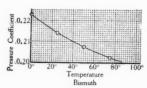


Figure 24. Bismuth, the average pressure coefficient between 0 and 12000 kg. as a function of temperature.

the coefficient of "analytically" pure bismuth (i. e. bismuth prepared chemically and known to contain some impurity) the impossibly high value 0.0052. Lenard, discussing his value 0.00458 for electrolytic bismuth says that he found, "as did v. Aubel," that the temperature coefficient was constant between 0° and 100°. Lenard gives none of

<sup>21</sup> E. v. Aubel, Phil. Mag. 28, 332 (1889).
22 Ph. Lenard, Wied. Ann. 39, 619 (1889).
23 Ph. Lenard und J. L. Howard, Electrot. ZS. 9, 340 (1880).

the details of measurement; in view of his remark it is possible that he extrapolated as did Jaeger and Diesselhorst. On referring to v. Aubel it is found that he does indeed emphasize the constancy of the temperature coefficient, but that his numerical values show a consistent increase from 0.00412 between  $0^{\circ}$  and  $19.5^{\circ}$  to 0.00450 between  $0^{\circ}$  and  $99.7^{\circ}$ . It would seem, therefore, that the temperature coefficient of perfectly pure bismuth has not yet been definitely established, but that there is no reason to suspect that the electrolytic bismuth measured above contains enough impurity to sensibly affect the result under pressure.

For the pressure coefficient there is only one other determination, by Williams, <sup>13</sup> over a pressure range of 300 kg. at 0°. Within the limits of error he found the relation between pressure and resistance to be linear, and the coefficient to be  $\pm 0.04191$ . He does not give the temperature coefficient of his specimen, but states that it was a spiral of electrolytic bismuth from Hartmann and Braun. The initial value which I found above was 0.04153. It is significant that the impurer grades gave a higher initial coefficient; that of the Kahlbaum "K"

specimen was 0.0<sub>4</sub>21.

The distinctive features of the behavior of bismuth are as follows; the average pressure coefficient is positive, increasing in numerical value with increasing pressure and decreasing with increasing temperature, and the instantaneous coefficient at 0 kg. is nearly independent of the temperature, but at higher pressures it decreases at the higher temperatures. This last point means that as pressure increases the temperature coefficient of resistance decreases.

### GENERAL SURVEY OF RESULTS.

In Figure 25 are collected curves for all the metals measured, except Te, Bi, Sb, and Mg, giving the average pressure coefficient to 12000 kg. as a function of temperature. The most obvious and striking feature is the slight variation of coefficient with temperature; the variation is in all cases much less than the change of resistance itself. To see the significance of this, let us for the moment suppose that the coefficient is strictly constant with temperature. If this is true, the curve of resistance against pressure at any temperature may be obtained from that at any other temperature merely by changing the scale of the ordinates by the proper factor. It would therefore follow that the temperature coefficient of resistance would be strictly independent of

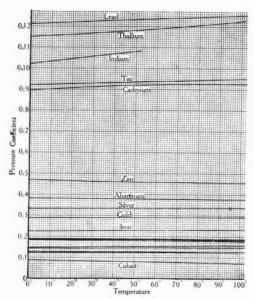


FIGURE 25. Collection of results, the average pressure coefficient between 0 and 12000 kg. as a function of temperature. The seven curves in the lower part of the diagram without labels are, reading upwards, for tungsten, molybdenum, tantalum, nickel, copper, platinum, and palladium.

pressure. As a matter of fact, the temperature coefficient of all substances is only slightly different at 12000 kg. from its value at 0 kg. Now, dropping the condition of invariability, it is easy to see that if the pressure coefficient of resistance increases at higher temperatures the temperature coefficient will be less at higher pressures, and viceversa. In Table XXII are collected the average temperature coefficients between  $0^{\circ}$  and  $100^{\circ}$  at 0 and 12000 kg. for all the substances for which the data have been obtained. Except for the abnormal metals, the slight change in temperature coefficient is striking.

The meaning of a temperature coefficient independent of temperature may be stated in another way. Let us compare at 0° and 100° respectively the slope of the lines on which resistance is constant with those on which volume is constant. Since it is a matter of experiment

that the compressibility and thermal expansion of most metals change relatively little between 0° and 100°, the slope of the constant volume line will be nearly independent of temperature. Since furthermore the relation between temperature and resistance is nearly linear for

TABLE XXII.

Average Temperature Coefficients between  $0^{\circ}$  and  $100^{\circ}$  at  $0\,$  kg. and  $12000\,$  kg.

	Average Ter	np. Coefficient
Metal	At 0 kg.	At 12000 kg
In	.00406	.00383
Sn	447	441
Tl	517	499
Cd	424	418
Pb	421	412
Zn	416	420
Al	434	435
Ag	4074	4069
Au	3968	3964
Cu	4293	4303
Ni	4873	4855
Co	3657	3676
Fe	6206	6184
Pd	3178	3185
Pt	3868	3873
Mo	4336	4340
Ta	2973	2967
W	3219	3216
Sb	473	403
Bi	438	395

most metals between  $0^{\circ}$  and  $100^{\circ}$ , the actual change in resistance in ohms of a given piece of wire will be the same for  $1^{\circ}$  rise of temperature at  $100^{\circ}$  as at  $0^{\circ}$ . But since the pressure coefficient is approximately constant, the change of resistance for 1 kg. will therefore, be greater at  $100^{\circ}$  than it is at  $0^{\circ}$  in the ratio of the resistance at  $100^{\circ}$  to that at  $0^{\circ}$ . For most metals this is of the order of  $40^{\circ}$ //0 difference. Therefore the slope of the line at constant resistance is greater at  $100^{\circ}$  than at  $0^{\circ}$ .

Since ordinarily the line of constant volume has a greater slope than that of constant resistance, it will result that at higher temperatures the two lines approach each other. If this tendency persists, it means that at high enough temperatures the resistance of a solid will decrease instead of increase along a line of constant volume with increasing temperature. This is an important point for theoretical considerations.

To a closer degree of approximation the pressure coefficient is not independent of temperature. The manner of dependence is plainly obvious from Figure 25; the coefficient may rise or fall with temperature. Furthermore, the relation between coefficient and temperature need not be linear; there are six examples of non-linear relation, Tl, Cd, Zn, Al, Ag, and Cu. The departure from linearity is so slight that it is not obvious on the scale of Figure 25. As a general rule, the coefficient increases with temperature for metals of low melting point, and decreases for those with higher melting points, although there are several exceptions. Except for this, there seems no obvious connection between the manner of departure from constancy and other physical properties.

At any constant temperature the relation between pressure and resistance is not linear, but the slope of the resistance-pressure curve becomes less at the higher pressures. This is true without exception for all the metals with a negative pressure coefficient, and is only what one would expect. The manner of departure from linearity varies from metal to metal, however. The variation is not regular, so the simple types of formula hitherto proposed to represent the dependence of resistance on pressure cannot be valid. There is a general tendency, however, for the maximum departure from linearity to be greater for those metals with the larger coefficient, as one would expect. Furthermore, the ratio of the maximum departure from linearity to the pressure coefficient is also greater for the greater coefficients. This means that as the effect of pressure on resistance increases from metal to metal, the relative curvature of the resistance-pressure curves increases also. This ratio is roughly proportional to the value of the pressure coefficient, as is shown by Figure 26, but there are several well marked exceptions, particularly at the smaller coefficients.

For any one substance, the variation with temperature of the ratio to the pressure coefficient of the maximum departure from linearity with pressure is of interest. This has already been mentioned under the individual substances: a curve with greater curvature at the higher temperature means a larger value for the ratio. The facts are a trifle

surprising here; for Pb, Tl, In, and Sn, the substances with the largest average pressure coefficient, the curvature is greatest at the highest temperature, but for all other normal substances it is less. For some substances, such as cobalt, the magnitude of the variation is surprisingly large; half the relative curvature disappears between  $0^{\circ}$  and  $100^{\circ}$ . This effect, although small, cannot be explained by errors in the pres-

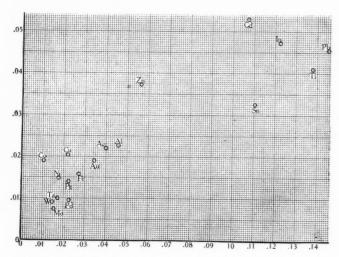


FIGURE 26. The ratio, at 0°, of the maximum departure from linearity to the change of resistance under 12000 kg. plotted against the change of resistance under 12000 kg. The diagram shows that in general the relative curvature of the resistance-pressure curves increases as the absolute value of the pressure coefficient increases.

sure measurements, because it will be remembered that the manganin measuring coil was always at the same temperature.

The position of the pressure of maximum deviation from linearity is another characteristic datum; this has already been tabulated under the individual substances. This pressure shows a distinct tendency to fall below the mean pressure, that is, below, 6000 kg. This is as one would expect if the instantaneous pressure coefficient tends toward constancy, that is, if the equation of resistance against pressure can be written  $R=R_0e^{-ap}$ . As a matter of fact, if the equation could be

written in this form, the pressure of maximum deviation would be approximately 3000 instead of 6000 kg. The closest approach to it is by Au and Cu at 0°, for which the pressures of maximum deviation are 4440 and 4200 respectively. The fact that the pressure of maximum deviation is so much above 3000 kg. for most metals means that the instantaneous coefficient becomes markedly less at the higher pressures. This is brought out in Table XXIII, in which the instantaneous

TABLE XXIII.

Comparison of Instantaneous Pressure Coefficient at  $0^{\circ}$  and 0 kg with that at  $0^{\circ}$  and 12000 kg.

Metal	Instantaneous Pressure Coefficient at 0°.			
	At 0 kg.	At 12000 kg		
In	04123	04102		
$\operatorname{Sn}$	04104	$0_{5}936$		
Tl	$0_{4}132$	04118		
$\operatorname{Cd}$	04106	05837		
Pb	04144	$0_4122$		
Zn	$0_{5}540$	$0_{5}425$		
Al	$0_{5}416$	$0_{5}365$		
Ag	$0_{5}358$	$0_{5}321$		
$\mathbf{An}$	$0_{5}312$	$0_5286 \\ 0_5179$		
Cu	$0_{5}201$			
Ni	$0_{5}158$	$0_{5}142$		
Co	$0_6941$	$0_6814$		
Fe	$0_{5}241$	$0_{5}218$		
Pd	$0_{5}198$	0,190		
Pt	$0_{5}1975$	0,181		
Mo	$0_{5}133$	$0_{5}126$		
Ta	$0_{5}149$	$0_{5}139$		
W	0,128	0,121		

coefficients at 0° are compared at 0 kg. and 12000 kg. The instantaneous coefficient at 12000 kg. was obtained by dividing the value already given in the tables by the resistance at 12000. Such a decrease of pressure coefficient with pressure is perhaps surprising after finding the constancy under pressure of the temperature coefficient. The displacement of the pressure of maximum deviation towards higher

pressure at the higher temperatures means that at higher temperatures the instantaneous pressure coefficient decreases more rapidly with increasing pressure than at lower temperatures. This comes to much the same thing as the statement that the curvature is less at the higher temperature, although the two statements are not entirely coextensive. The rate at which the pressure of maximum deviation is displaced at higher temperatures is very different for various substances and seems to have no obvious connection with other properties.

To sum up: different metals show minor irregularities in behavior, but they are alike in several general features which must be the first task of any theory to explain. These general features are the approximate constancy of pressure coefficient with temperature, and the accompanying constancy of temperature coefficient with pressure; contrasted with this the pronounced decrease of instantaneous pressure coefficient with rising pressure, and, of less compelling importance, the decrease in the curvature of most of the resistance-pressure curves at higher temperatures.

Bearing of the Results on the Question of the Metastability OF THE METALS.

In the last few years a great deal of work has been done by Cohen 24 and his pupils on the variation in the behavior of metals after different kinds of heat treatment. They have found very small discontinuities in various physical properties which have been interpreted as indicating that a number of the metals occur in several polymorphic forms. Similar discontinuities have also recently been found by Jänecke, <sup>19</sup> but almost always at higher temperatures. The existence of such modifications is important both from the practical point of view and because of the intimate relation to the theory of allotropy of Smits.<sup>25</sup> Cohen's result for copper has recently been called in question by Burgess and Kellberg, 26 who could find no discontinuity in the electrical resistance in the expected place.

The results above throw light on the same question. If there are polymorphic transitions, there should be discontinuities in the resist-

<sup>24</sup> E. Cohen, Numerous papers in Proc. Amst. Acad. since 1913.

 <sup>25</sup> A Smits, Proc. Amst. Acad., numerous papers 1910–15.
 26 G. K. Burgess and I. N. Kellberg, Jour. Wash. Acad. Sci. 5, 657–662 (1915).

ance, and the discontinuity should be at different pressures at different temperatures. The metals for which such discontinuities should be expected between 0° and 100° are Cd, Pb, Cu, Zn, and Bi, according to Cohen. No such effects were found. The sensitiveness of the measurements may be estimated from the data already given: the accuracy is in most cases great enough so that a discontinuity of the order of 1/100% of the total resistance could have been detected. According to Jänecke, however, the transitions all occur above 100°, and none should have been found under pressure, if the phase stable at the higher temperature has the greater volume. I did find a discontinuity at 140° for antimony, which is much nearer the value of Jänecke than of Cohen. This has already been discussed. One of the metals examined is certainly known to have a transition in the temperature range 0° to 100°, tin at 20°. But the transition never starts under ordinary conditions, and one need not expect to find it under pressure. This has already been made the subject of a special investigation.27

In criticism of the results, one may well admire the skill and care which Cohen and his pupils have bestowed on the measurement of these very minute effects; the existence of the discontinuities which they have found may doubtless be accepted. But it seems to me that their interpretation of the results may well be questioned; the existence of a discontinuity, more or less indefinite, need not of itself be an indication of true polymorphism. It seems that there are many possibilities in the rearrangement of crystalline grams or growth of the larger crystals at the expense of smaller ones (such as have been found by Ewing and Rosenhain 28 to be stimulated by strains), and that these possibilities of explanation should first be exhausted. The facts that different observers find different transition points and that it is in almost every case necessary to assume more than two modifications to explain the results lend color to suspicion. Furthermore, if the discontinuities are truly polymorphic in character, there was the best possible chance to detect them under pressure, but none were found. Before the interpretation assigned by Cohen to the results can carry conviction, it would seem to me that we have a right to ask for reproducible results with large individual crystals. It would be worth much effort to prepare such crystals in order to settle this vexed question.

<sup>27</sup> P. W. Bridgman, Proc. Amer. Acad. 52, 164 (1916).
28 J. A. Ewing and W. Rosenhain, Phil. Trans. (A), 353 (1900).

# THEORETICAL BEARINGS.

Before discussing the bearing of these results on electron theories of metals, it will pay to emphasize two points. The first is that the coefficients tabulated are the actual observed coefficients, measured by the ordinary methods with electrodes permanently fixed to determinate parts of the surface. But in theoretical discussion we are more inclined to be interested in the variation of specific resistance. To get this, the observed results must be corrected by a factor equal to the change of linear dimensions. It is easy to see that for normal metals the temperature coefficient of observed resistance is numerically smaller than the temperature coefficient of specific resistance by the linear thermal dilatation, and the pressure coefficient of observed resistance is numerically less than the pressure coefficient of specific resistance by the linear compressibility. This factor is not important for the temperature coefficient, rising in the extreme case above (In) to 1%, but for the pressure coefficient it may amount to 10% in some cases. In making correction for the compressibility we are confronted by the difficulty that only one or two compressibilities have been measured over any extensive pressure range. For the initial compressibility we have the data of Richards;29 at higher pressures the best that we can do is to neglect the change of compressibility with pressure. For the less compressible metals any such change is probably slight. A number of years ago I measured the compressibility of iron up to 10000 kg. and of aluminum to 6500 kg., and could find no variation over this range.30 Of course in any discussion of the pressure coefficient of specific resistance at atmospheric pressure this source of uncertainty does not enter.

The second observation is concerning the magnitude of the effects. It has been obvious enough that the data have presented no spectacular features, and I must confess to a sense of disappointment that an extension of the pressure range to at least four fold that of previous measurements has brought out no striking new facts to reward the extra effort. It is true that as far as I am aware the independence of temperature coefficient and pressure was not previously known, or at least was never emphasized, but it might have been discovered by measurements to only 3000 kg. if one had been willing to take the trouble.

 $<sup>29\</sup> T.\ W.\ Richards, Jour.\ Amer.\ Chem.\ Soc.\ 37, 1643-1656\ (1915).$   $30\ P.\ W.\ Bridgman,\ Proc.\ Amer.\ Acad.\ 44, 255-279\ (1909)\ and\ 47, 366\ (1911).$ 

When the magnitude of the change of volume produced by a pressure of 12000 kg. is considered, however, it does seem that the results acquire a physical significance great enough to justify the extension of the range. The volume of many of the metals at 0°C and 12000 kg. is less than the volume at atmospheric pressure at 0° Abs. The resistance of most metals tends towards zero at 0° Abs., but at 0° C at the same volume the resistance is only a few per cent less than under normal conditions. Any valid theory must explain the surprisingly little effect of the element of volume alone apart from the element of temperature. It is furthermore known that at very low temperatures the connection between resistance and temperature changes its character; the relation ceases to be linear, and the resistance curve approaches the origin tangentially to the temperature axis. Whether the abrupt discontinuity shown by several metals a few degrees above 0° Abs. is an effect of a polymorphic transition does not yet seem to be settled. It is significant that no trace of any such effect is to be found at room temperature as the volume is decreased toward and beyond its value at 0° Abs. The question whether there is a change in the character of the resistance curves as the volume approaches that at 0° Abs. could not, of course, have been answered by measurements over a small pressure range; it is perhaps some justification of the extension of range that this question can now be answered.

An estimation as to the comparative volumes at (12000 kg., 0°C) and (0 kg., 0° Abs.) is given in the accompanying Table XXIV. The values of compressibility used in the computations have been taken from Richards 29, assuming constancy over the pressure range, and the volume at 0° Abs. has been taken from the data of Ch. Lindemann 31 on linear expansion to 20° Abs. The Table includes all the metals measured by Lindemann to 20°. Linear extrapolation of data of Grüneisen 32 to liquid air temperature shows that tin and magnesium also have a smaller volume under 12000 kg. than at 0° Abs., and probably iron does also. The two metals antimony and bismuth which are abnormal with respect to pressure coefficient are also abnormal here; the decrease of volume under 12000 kg. is more than three times as

great as that on cooling to 0° Abs.

Let us now consider the bearing of the facts at high pressures on various proposed theories of electronic conduction in metals. We discuss first their relation to the classical gas-free-electron theory of

<sup>31</sup> Ch. L. Lindemann, Phys. ZS. 12, 1197-1199 (1911). 32 E. Grüneisen, Ann. Phys. 33, 33-78 (1910).

### TABLE XXIV.

Comparison of Changes of Volume produced by Temperature and Pressure.

Metal	Change of volume between 0°C. and 0°Abs at at 0 kg.	Change of volume between 0 kg. and 12000 kg. at 0°C.		
Pb	.0189	.0275		
Zn	.0057	.0200		
Al	.0096	.0173		
Ag	.0108	.0119		
Cu	.0078	.0089		

Riecke, Drude, and Lorentz. The specific resistance according to this theory is given by

$$w = Const \frac{u}{Nl} = Const' \frac{T^{\frac{1}{2}}}{Nl}$$

where u is the velocity of the electrons, l their mean free path, and N the number per cm<sup>3</sup>. The constant has different numerical values according to Drude and Lorentz. The second form of the equation is obtained by putting  $u^2$  proportional to T.

Apart from specific heat difficulties, which it seems to me have been over-emphasized, this theory has always had difficulty in giving a plausible explanation of the variation of resistance with temperature, it being necessary to suppose that l decreases as the volume increases with rising temperature. But since the mean free path is supposed entirely determined by the positions of the atoms, these being immobile compared with the free electrons, the hypothesis of decreasing l is difficult. A suggestion as to a way out is by considering the collisions among the electrons themselves; there may be a more than proportional increase in the number of such collisions as the space between the atoms becomes larger. But this possibility is removed when we consider the changes at constant volume. It is a result of these

experiments that if a metal is warmed from  $0^{\circ}$  Abs. and pressure is simultaneously applied so as to keep the volume constant, that the change of resistance is very nearly the same as if the metal were allowed to expand freely when heated. But under heating at constant volume, the mean free path according to the fundamental point of view must remain constant, and we can explain the facts only by supposing N to decrease proportionally as  $\sqrt{T}$  increases. Such a hypothesis is to say the least improbable.

The classical theory also meets difficulties in explaining the negative pressure coefficient of resistance at constant temperature. As volume decreases with increasing pressure at constant temperature, the mean free path must decrease, and the decreased resistance can be accounted for only by an increase in N. But from work by Wagner <sup>33</sup> on the effect of pressure on thermo-electromotive force, it appears that N

must decrease slightly as pressure increases.

Dismissing, then, the gas-free-electron theory, we consider several of the recent attempts to improve upon it. Perhaps the most radical of these is the recent revival by J. J. Thomson <sup>34</sup> of a theory of his dating back to 1888, in which he assumed the atoms of a metal to be electric doublets continually emitting and absorbing electrons along their axes. In an electric field there is a resultant orientation in the direction of the field which gives rise to the current. This theory has many formidable difficulties, in fact it seems in certain aspects almost grotesque, but as Lees <sup>35</sup> has remarked, it seems to offer possibility of at least qualitative solution of many of the problems before which the older theory was helpless, and therefore should not be cast lightly aside. It is interesting to see what account this gives of the variation of resistance with pressure. At not low temperatures the formula for conductivity is

$$C = \frac{1}{3} \frac{NepdM}{kT}$$

where N is the number of doubtlets per cm<sup>3</sup>, e electronic charge, p the number of electrons emitted by an atom per second, d the distance between centers of adjacent atoms, M the moment of the doublet, and k the gas constant. If now pressure is increased at constant temperature, d and M must both decrease, if anything, because of the change

<sup>33</sup> E. Wagner, Ann. Phys. 27, 955–1001 (1908).
34 J. J. Thomson, Phil. Mag. 30, 192–202 (1915).
35 C. H. Lees, Nat. 95, 675–677 (1915).

of dimensions. N will increase for the same reason, but this increase is sufficient to account for not over 25% of the effect. Hence most of the increase of conductivity must be due to an increase in p. Now this is a most unfortunate member to call on to do the brunt of the work, because it is already sorely overburdened. In fact, one may calculate p from data in a recent paper of Richardson  $^{36}$  for tungsten at  $2000^\circ$ . It turns out that p is about  $1.7\times10^{16}$ . Since the figures given by Richardson lead to a minimum value of p it seems evident that parts of the theory must be radically recast. I owe the idea that p is improbably large to a remark of Professor E. H. Hall.

Another recently suggested theory which seems to have possibilities is that of F. A. Lindemann.<sup>37</sup> According to this theory the electrons are rigidly arranged in the nodes of a space lattice between the atoms. The state of the electrons is therefore that of a perfect solid rather than of a perfect gas. Since however this theory gives essentially the same account of pressure effects as does Wien's recent theory as modified by Grüneisen, we may omit special discussion of this and pass to

the Wien-Grüneisen theory.

The only serious attempt that has been made to bring pressure effects within the range of an electron theory has been by Grüneisen. His starting point is the theory of Wien, who supposes that the electron velocity is independent of temperature. With this assumption, combined with assumption of the quantum distribution of energy. Wien finds a function proportional to the mean free path. Starting with Wien's value of the free path, which he "generalizes", and with the help of his theorem that along a line at constant entropy T remains constant, Grüneisen finds a value for the pressure coefficient in terms of quantities most of which are known. There is reason to except that the unknown quantities are not as important as the others, and by neglecting them a formula is obtained for pressure coefficient in terms of compressibility, thermal expansion, specific heat, and temperature coefficient of resistance. The formula follows;

$$\frac{1}{w} \left( \frac{\partial w}{\partial p} \right)_{t} = \frac{1}{u} \left( \frac{\partial u}{\partial p} \right)_{s} - \frac{1}{N} \left( \frac{\partial N}{\partial p} \right)_{s} - \frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_{s} - \frac{1}{Cp} \left( \frac{\partial v}{\partial T} \right)_{p} \left[ 1 + \frac{1}{w} \left( \frac{\partial w}{\partial T} \right)_{p} T \right].$$

The first two terms, which represent the change of electronic velocity

O. W. Richardson, Phil. Mag. 30, 295–299 (1915).
 F. A. Lindemann, Phil. Mag. 29, 127–140 (1915).
 W. Wien, Columbia Lectures, (1913), p. 29.

with pressure at constant entropy, and the change in the number of free electrons, may be neglected. Grüneisen compares his formula with experiment with surprisingly good results; in many cases the agreement is within the limits of error, and the worst discrepancy is for lead, where the difference is 50%. More recently Beckman<sup>6</sup> has extended the range of experimental material, and has applied Grüneisen's formula to all the available data. He concludes that the formula cannot be considered exact, but must be regarded only as an approximation. Grüneisen himself certainly did not claim more.

The new material of this paper allow a comparison with Grüneisen's formula over a somewhat wider range. Furthermore, since the numerical values found in this paper often differ considerably from those of Beckman, I have thought it worth while to recompute all the data. The results are shown in Table XXV. In the recomputation I have used my own values for the pressure coefficient and also for the temperature coefficient, except in several cases where higher values have been reported by other observers. In the recomputation I have paid attention to several minor points. For the temperature coefficient of resistance I have used the coefficient of specific resistance (which is strictly correct) instead of the coefficient of observed resistance. The difference is only a fraction of a per cent. Furthermore, I have used the instantaneous coefficient at 0° where the data are available, instead of the average coefficient between 0° and 100°. This again is the strictly correct procedure; for most substances it makes little difference, but for iron the difference is 8.5%. It must be recognized, however, that there are much greater uncertainties in the fundamental data entering the equations than can be introduced by the nicer points just mentioned. I have taken the fundamental data, except pressure and temperature coefficient, from the last edition of Landolt and Bornstein, selecting the values that seemed most consistent. I have given the preference to the values of specific heat of Jaeger and Diesselhorst at 18°. For zinc I have used the value of the thermal expansion of the National Physical Labaratory, 0.0478. There is much discrepancy for this substance between different observers; Grüneisen's own experimental value, 0.0451, seems certainly too low. The expansion of cadmium also is variously given; I adopted 0.0490 as a mean between Dorsey, 0.04881, and Fizeau, 0.0493. The expansion of molybdenum and tungsten were taken from the Tables of the French Physical Society. It is to be noticed that the  $C_p$  in Table XXV is in kg. cm. per cm<sup>3</sup> of material. The compressibility of indium has been assumed to be  $2.0 \times 10^{-6}$ , in

TABLE XXV.

Pressure Coefficient of Specific Resistance Calculated by Grüneisen's formula.

Metal	Compressibility $-\frac{1}{v} \left( \frac{\partial v}{\partial p} \right)_{\tau}$ in kg	Expan- Consion S	Temp.	Specific Heat C <sub>p</sub> kg. cm. per cm <sup>3</sup>	Pressure Coefficient of Specific Resistance		
			Coeff. of Specific Resist- ance at 0°C		Computed Grüneisen	Observed	Computed by Beckman with G's formula
In	2.0(?)×10 <sub>6</sub>	.0313	.00404	17.5	04137 ?)	04129	
Sn	1.86	.0451	433	17.2	$.0_{5}464$	.041106	0.05672 0.0582
Tl	2.26	.0492	520	16.4	.04113	.04139	
Cd	2.06	.0490	407	20.3	$.0_{5}728$	.041132	(.0571
Pb	2.28	.04879	409	14.9	.04102	.04152	(.0 <sub>5</sub> 98 (.0 <sub>4</sub> 104
Zn	1.66	.0478	407	27.8	.0s427	$.0_{5}595$	.05488 .05276
Mg	2.84	.0478	396	18.3	.05601	$.0_{5}55$	
Al	1.44	.0474	433	24.1	.0536	.05464	.05423
Ag	.99	.0455	406	24.9	.05372	$.0_{5}383$	.05384
An	.63	$.0_{4}43$	392	25.6	.05292	$.0_{5}333$	.05279
Cu	.735	$.0_{4}51$	431	35.2	.05241	$.0_{5}245$	$.0_{5}211$
Ni	.42	.04375	62	40.9	$,0_{5}206$	$.0_{5}172$	(.0 <sub>5</sub> 193 (.0 <sub>5</sub> 157
Co	(.50)(?)	.0437	366	37.8	.05146(?)	.05110	
Fe	.58	.04375	562	35.3	.05210	$.0_{5}260$	.05177
Pd	. 53	.04355	322	30.0	.05171	$.0_{5}216$	.05202
Pt	.27	.04292	388	29.3	$.0_{5}179$	.05207	.05150
Mo	.45	.04108	435	24.8	$.0_{6}50$	$.0_{\delta}148$	
Ta	. 52	.04237	298	23.1	$.0_{5}135$	$.0_5166$	
W	. 265	.04101	318	27.7	$.0_{6}42$	$.0_{\delta}137$	

absence of measurements, as fitting well into the periodic table as shown by Richards. <sup>29</sup> Also the compressibility of cobalt has not been measured; I have assumed a mean between iron and nickel.

For comparison, the computed values of Beckman, reduced from atmospheres to kilograms, are reproduced in Table XXV. It appears that the revised values sometimes give better and sometimes poorer agreement with theory: Beckman's conclusion need not be altered, therefore.

A mere comparison of the approximate formula with experiment is not at present sufficient to show, however, the correctness of Grüneisen's fundamental assumption, because the formula is obtained by neglecting an unknown term,  $\frac{1}{u} \left( \frac{\partial u}{\partial p} \right)_s$ , whose presumptive magnitude might possibly be  $\frac{1}{4}$  of the entire effect. It therefore is pertinent to consider the nature of the assumptions which Grüneisen has put into his theory. The general nature of the underlying idea is as follows. It was a cardinal point of Wien's theory that the length of the free path is determined by the motions of the atoms; at higher temperatures the amplitude of atomic vibration becomes greater, and so interferes more with the freedom of electronic motion and decreases the free path. The sign of the pressure effect is explained by showing that as pressure increases at constant temperature the decrease of amplitude of atomic vibration in virtue of the increased frequency more than counterbalances the decreased distance between atomic centers due to volume compression, so that free path, and therefore conductivity, increase. The starting point of Wien's theory is the formula already given, Wien assumes that u and N are both independent of temperature. It is to be noticed, however, that Wien was concerned only with temperature effects, and for these, as already mentioned, changes of volume may be neglected. Wien's hypothesis that N is constant must not therefore be understood as committing Wien to the statement that when changes of volume are considered the number of free electrons per cm3 is constant. On the contrary, it is clearly suggested, although not explicitly stated, that Wien meant the number of electrons per gm. to remain unaltered. This would mean that Nv is constant. Certainly in the absence of any special examination of the effects of varying electronic dissociation, this is the only plausible hypothesis to make. Now in Grüneisen's deduction of the formula he has not assumed either that N or Nv is constant, but has left N in the equation and differentiates it, and arrives at a formula containing  $1/\partial N$ This he assumes can be neglected in numerical magnitude  $N(\partial p)_s$ on the basis of experiments of Wagner 33 on the effect of pressure on thermo-electromotive force. But the calculation of  $\frac{1}{N} \left( \frac{\partial N}{\partial p} \right)_s$  from

Wagner's data proceeds on the assumptions of the gas-free-electron

theory. One cannot grant that it is permissible to mix in the same equation two theories so opposed in fundamentals. If Grüneisen had assumed Nv constant, which seems the only defensible course until an explanation of thermo-electromotive force is provided on the basis of Wien's theory, the compressibility terms would have disappeared from his formula, with a change in the numerical value of 25%.

A criticism of Wien's fundamental point of view is pertinent here. His calculation of the mean free path proceeds on the assumption that the quanta of energy are located in the individual atoms, instead of in the elastic waves, which at present seems to be the accepted conception. It is evident that this change will considerably modify the physical picture of the manner in which the vibrating atoms interfere with the motion of the electrons, and might be expected to modify the result.

Another consideration vital to Grüneisen's theory is the way in which he has "generalized" Wien's expression for the free path. Grüneisen's expression is

$$\frac{1}{l} = Const \frac{h}{M\nu_m v} f\left(\frac{T}{\beta\nu_m}\right).$$

The important feature about this generalization is the appearance of the atomic volume v. The volume does not enter in the considerations of Wien; its introduction must have been part of Grüneisen's process of generalization. It is unfortunate that he gives none of the argument by which he reaches the above expression, because the factor v is important, contributing 25% of the total effect, and its appearance in the place where it is involves definite hypotheses about the atomic mechanism. If the free path is proportional to the volume, other things being equal, and if the free path is determined entirely by the vibrations of the atoms, as is supposed in this theory, then the atoms must behave effectively like mathematical points, and not as if they had extension in space. Such a hypothesis is at least opposed to the present view of the nature of the atoms in a solid and would seem to require discussion.

As it now stands, therefore, the theoretical basis for Grüneisen's formula requires elaboration in several particulars. But it must not be forgotten that for a first attempt at an explanation of the pressure effect the formula works surprisingly well and must contain a considerable element of truth. It seems to me that the element of truth is to be found essentially in the broad change in the fundamental

point of view introduced by Wien, namely in considering the phenomena of conduction to be primarily determined by the motions and properties of the atoms of a metal, and not by the properties of the swarm of electrons playing in the spaces between inert atoms. I hope to show in a future paper that a somewhat different physical account can be given of the phenomena, still retaining Wien's broad view point, and that the formulas so obtained are somewhat like those of Wien in general character and are in better agreement with the facts.

# SUMMARY.

In this paper data are given for the change of resistance of 22 metals between 0° and 100°C over a pressure range from 0 to 12000 kg. Three of the metals are abnormal; bismuth and antimony both have a positive pressure coefficient, and the pressure coefficient of tellurium has an abnormally large negative value. The other 19 metals have minute differences in their individual behavior, but in broad outline the behavior of all is alike. The pressure coefficient changes very little with temperature, and therefore also the average temperature coefficient changes very little with pressure; this holds over a range of pressure great enough in many cases to compress the metal to less than its volume at 0° Abs. under atmospheric pressure.

The instantaneous pressure coefficient of all the normal metals on the other hand decreases markedly with increasing pressure. By far the larger number of the normal metals show a decreased relative curvature in the resistance-pressure curve at the higher temperature.

It is shown that none of the hitherto proposed theories can satisfactorily account for all these facts. The recent attempt by Grüneisen, however, must be recognized as a promising beginning.

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